THE GAS PHASE THERMAL DECOMPOSITION OF BENZOIC ACID

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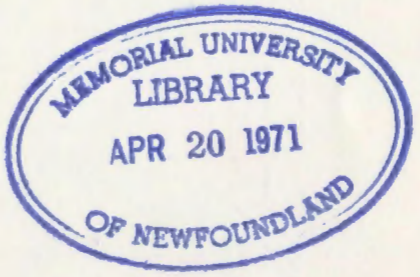
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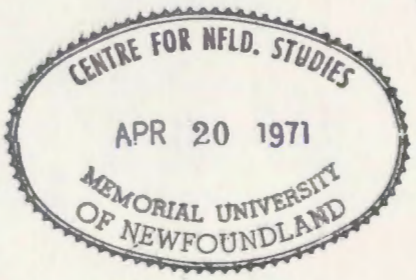
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THE GAS PHASE THERMAL DECOMPOSITION OF BENZOIC ACID

by

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ABSTRACT

The gas-phase thermal decomposition of benzoic acid has been investigated at 475.1, 486.0, and 498.5°C. The main reaction products were carbon dioxide and benzene. Carbon monoxide accounted for 5 to 20°/o of the total of carbon monoxide plus carbon dioxide, depending on whether or not a conditioning experiment was carried out prior to the reaction to be studied. Biphenyl and small quantities of hydrogen were also detected. The order of the carbon dioxide producing reaction was 1.25 while those of the reactions producing carbon monoxide and hydrogen were higher (tentatively second order). The Arrhenius equation for the production of carbon dioxide was

$$k = 10^{13.41} \exp(62{,}200/RT) 1.^{.25}_{\text{mole}}{}^{-.25}_{\text{sec.}}{}^{-1}$$

Reactions carried out in the presence of toluene $-d_8$ indicate that approximately 80°/o of the decomposition takes place by a molecular rearrangement. A free radical mechanism has been proposed to account for the remainder of the decomposition.

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INTRODUCTION

Studies of the gas phase thermal decomposition of carboxylic acids indicate that there are great differences in the manner in which the acids react. A brief survey should serve to point out the diverse nature of these reactions.

Formic Acid.

Blake and Hinshelwood[1] in their study of the formic acid decomposition found that the acid decomposed by one of the following two reactions

$$HCOOH \longrightarrow CO_2 + H_2$$

$$HCOOH \longrightarrow CO + H_2O$$

The rates of both decompositions were independent of surface/volume ratio in carbon coated silica vessels, when the ratio was increased by a factor of 8, at all formic acid pressures between 3 and 650 mm. Both decomposition reactions were found to display kinetics in carbon coated silica vessels that were considerably different from those in uncoated vessels.

Blake and Hinshelwood state that both reactions appear to be homogeneous and molecular and that there is no evidence that chain processes occur, the rate being unaffected by inhibitors such as propylene and isobutene. The rate was increased in the presence of nitric oxide

but reproducibility was poor. This increase in rate is suggested to be due to some surface effect since the authors claim that nitric oxide reacts with carbon at the temperatures studied (436-532°C). Maximum pressure of the inhibitor was of the order of 200 mm. (maximum ratio inhibitor/acid was 2, which is relatively low).

The reaction was also studied in the presence of added foreign gases: carbon monoxide, carbon dioxide, carbon tetrafluoride, hydrogen, and water vapour. Although these produced no difference in rate, trace amounts of oxygen caused a "considerable" increase in rate.

The rate constants for the two paths of decomposition were given as

$$k_{CO_2} = 10^{4.8} \text{ exp. } (-30{,}600/RT) \text{ sec.}^{-1}$$

(The carbon dioxide-producing reaction was found to be very nearly first order.)

$$k_{CO} = 10^{7.46} \text{ exp. } (-28{,}500/RT) \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

On the basis that, even at this temperature, formic acid contains a small proportion of dimer, they claim that the second order carbon monoxide-producing reaction could be interpreted as the unimolecular decomposition of dimer molecules. This, and the fact that dimerization of formic acid is exothermic to the extent of 14.1 kcal. mole^{-1}, allows them to restate the rate constant for carbon monoxide production in the form

$$k_{CO}^{dimer} = 10^{13.58} \exp. (-42{,}600/RT) \text{ sec.}^{-1}$$

If carbon monoxide is actually produced by the unimolecular decomposition of formic acid dimers the reaction has Arrhenius parameters usually associated with unimolecular reactions.

The ratio CO/CO_2 was found to be pressure-dependent and decreased steadily as the reaction proceeded. This is not too surprising since the reaction producing carbon dioxide is first order while that producing carbon monoxide is second order.

Since the pre-exponential factor is so small for carbon dioxide production Blake and Hinshelwood speculate on the existence of "ion-pairs", in the gas phase, decomposing to give carbon dioxide and hydrogen. They suggest that these ion pairs could be formed on the surface of the reaction vessel. This seems to contradict their assertion that the surface plays no part in the reaction.

The gas phase decomposition of formic acid has also been investigated by Watson[2] in carbon coated vessels. In this study a complete product analysis was undertaken to ascertain whether carbon dioxide and hydrogen, and carbon monoxide and water were produced in equimolar quantities as, indeed, they should be if the reactions are totally molecular. Isotopic studies using DCOOH and HCOOD were also undertaken to investigate the molecular

nature of dehydrogenation reaction. The dehydration could not be studied isotopically because of the occurrence of the exchange reaction

$$H_2O + D_2O \rightleftharpoons 2DOH$$

The reactions

$$H_2 + D_2 \rightleftharpoons 2HD$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

did not occur. Consequently dehydrogenation should produce only HD in a molecular reaction.

No mention is made of the possibility of

$$H_2O + D_2 \rightleftharpoons DOH + HD$$

This reaction would have the effect of raising the HD/H_2 ratio and lowering the D_2/H_2 ratio but could only occur if the decomposition of the deuterated acids was not molecular since, if the reaction were wholly molecular, istopically pure H_2O and D_2 would not be found in the products.

The HD/H_2 ratio found was nearly 1.2 and the D_2/H_2 ratio .5 and 1.4 for DCOOH. For HCOOD the ratio found for HD/H_2 was about 0.8 while D_2/H_2 was 0.2. These results lead to the conclusion that the reaction producing carbon dioxide and hydrogen is not purely molecular as proposed by Blake and Hinshelwood.

Acetic Acid

The gas phase thermal decomposition of acetic acid has been investigated by Bamford and Dewar[3] in a flow system over the temperature range 500-900°C. They found the two reactions

$$CH_3COOH \longrightarrow CH_2CO + H_2O$$

$$CH_3COOH \longrightarrow CO_2 + CH_4$$

to be first order when the decomposition was carried out in carbon-coated tubes. The results were very dependent on the surface condition of the reaction vessel but were found to be reproducible after a number of runs had been carried out without cleaning off the carbon which coated the walls of the tube from the decomposition of keten. It was found that packing the reaction vessel to increase the surface/volume ratio by approximately 15 times had no appreciable effect on the rate constant. The rate constant for the decomposition to carbon dioxide and methane appeared to decrease at pressures lower than 60 mm. in the packed tube. Bamford and Dewar did not investigate this phenomenon in the unpacked tube.

The activation energy and frequency factor for the reaction producing water and keten were 67.5 kcals. $mole^{-1}$ and 9×10^{12} $sec.^{-1}$ respectively. For the carbon dioxide and methane-producing reaction these parameters were 62 kcals. $mole^{-1}$ and 8×10^{11} $sec.^{-1}$ respectively. These frequency factors lie within the normal unimolecular

region.

The most striking feature in experiments without carbon coating the surface of the reaction vessel was the sharp increase in yield of keten. With the reaction vessel in this condition the overall conversion was also greatly increased. In the packed tube this increase was even greater.

They suggest that a surface process is involved since the order for the keten-producing reaction varies between zero and one in the clean vessel and that it must be a surface reaction rather than a surface catalysed chain reaction.

Since no appreciable changes in rate were observed on increasing the surface/volume ratio in carbon-coated vessels, Bamford and Dewar contend this is indicative of homogeneity in the reactions producing keten and water, and carbon dioxide and methane in this case. This is not unreasonable.

Isotopic studies with acetic acid, deuterated at the three methyl hydrogens and with normal hydrogen on the carbonyl group, and vice versa, after the manner employed by Watson[2] in the previously mentioned formic acid study, would have been useful in establishing the extent of any free radical process. Experiments similar to those described later in this work and studies of the effects of inhibitors would also have aided in this investigation.

Trifluoroacetic Acid

Blake and Pritchard[4] believe that the decomposition of trifluoroacetic acid is not a chain reaction on the basis of results obtained in experiments in the presence of nitric oxide. Nitric oxide was found to have no effect other than to increase slightly the amount of carbon dioxide produced.

Three reaction vessels were used; a mild steel vessel which was previously washed with anhydrous HF, and two silica vessels, one of which was packed. It was found necessary to condition all three vessels by repeatedly decomposing trifluoroacetic acid. The conditioning produced constant rates in the two silica vessels but produced slowly but continually decreasing rate constants in the steel vessel. Orders were generally less than 0.5 in all vessels at 340° and rose towards unity with increasing temperature.

Isobutene appeared to cause some inhibition but this was discounted on the grounds that trifluoroacetic acid adds readily to olefins to give esters. Because of this addition they place more emphasis on the nitric oxide results than on those obtained with isobutene.

The effect of traces of oxygen present in the reaction vessel were also reported: 5°/o O_2 caused a 12°/o increase in the rate of pressure increase, after a short induction period. However, the only large change

in products was an increase in the percentage of COF_2.

Blake and Pritchard's results suggested to them that the decomposition was partly heterogeneous with, perhaps, a homogeneous component which became more important with increasing temperature.

The products, in decreasing order of importance, were CO_2, CF_3COOCF_2H, CO, CF_3COF, and H_2O. Minor amounts of CF_3H, COF_2, SiF_4, and C_2F_4 were also reported. The products reported eliminate the reaction

$$CF_3COOH \longrightarrow CF_3H + CO_2$$

as a major contributor to the decomposition. The presence of SiF_4 was thought to be due to attack by HF on silica.

They state that rates in the packed vessel (an increase in surface/volume ratio of about 13.5) were less than half those in the unpacked vessel but were unable to explain this since they believed free radical chains to be absent. Since the ratio pressure of inhibitor/pressure of acid given for the nitric oxide experiment was quite low (0.09), possibly much higher ratios would cause noticible inhibition.

Activation energies for formation of carbon dioxide, carbon monoxide, and difluoromethyl trifluoroacetate were given as 48, 43, and 43 kcal. $mole^{-1}$ respectively and the following mechanism was proposed

$$CF_3COOH \longrightarrow HF + CF_2CO_2$$

$$CF_2CO_2 \longrightarrow CF_2 + CO_2$$

$$CF_2CO_2 \longrightarrow COF_2 + CO$$

$$CF_2 + CF_3COOH \longrightarrow CF_3COOCF_2H$$

$$HF + CF_3COOH \longrightarrow CF_3COF + H_2O$$

Propionic Acid

Blake and Hole[5] found that the decomposition of propionic acid was independent of surface/volume ratio in carbon-coated vessels. The decomposition takes place predominantly by a second order reaction giving methylketen and water represented by the Arrhenius equation

$$k = 10^{8.76} \text{ exp. } (-35{,}150/RT) \text{ l. mole}^{-1}\text{sec.}^{-1}$$

A first order reaction producing carbon dioxide, ethane, and ethylene also occurs, its Arrhenius equation being

$$k = 10^{9.78} \text{ exp } (-49{,}300/RT) \text{ sec.}^{-1}$$

Methylketen further decomposed to carbon monoxide, carbon dioxide, and hydrocarbon products, the formation of tars was also observed. Thus, methylketen became a relatively minor product at high temperatures.

On increasing the surface/volume ratio by a factor of nearly 7, the rate of propionic acid decomposition was found to increase by 15°/o but this was claimed to be negligible. The order for the rate of decomposition of acid fell steadily from 1.8 at 496.6° to 1.4 at 580°C. That for the formation of water remained at 2 with respect

to acid at all temperatures studied.

The effects on the rate of reaction due to isobutene, nitric oxide, hydrogen, biacetyl, and carbon dioxide were examined. Isobutene reduced the rate of acid decomposition and carbon dioxide formation but increased water and carbon monoxide production. Nitric oxide results were not reproducible; an effect explained by attack on the carbon surface of the reaction vessel by nitric oxide. Biacetyl greatly increased the rate of acid decomposition and, to a lesser extent, the rate of water formation. The addition of excess carbon dioxide caused no change in rate; indicating that no collisional effect contributed to the aforementioned rate increases.

Blake and Hole contend that these results indicate that the decomposition is a chain process. The following mechanism is proposed

$$C_2H_5COOH \longrightarrow C_2H_5\cdot + .COOH$$

$$.COOH \longrightarrow CO_2 + H.$$

$$H. + C_2H_5COOH \longrightarrow H_2 + .C_2H_4COOH$$

$$.C_2H_4COOH \longrightarrow C_2H_4 + .COOH$$

$$H. + .COOH\ (+M) \longrightarrow HCOOH\ (+M)$$

The reported discovery of formic acid in the products is surprising considering the temperature at which this work was carried out (496-580°C). It is not stated whether the formic acid was found at all temperatures

studied or just at the lower end of the temperature range. The formic acid would be expected to decompose preferentially to carbon monoxide and water[2] with some hydrogen and carbon dioxide produced as well. This latter mode of decomposition would contribute to the small amount of hydrogen being formed. However, since only small amounts of hydrogen were detected, reactions leading to its production can likely be neglected. No suggestions are made as to the mode of water formation.

3- Butenoic Acid

According to Smith and Blau[6] the thermal decomposition of 3- butenoic acid follows first order kinetics. The rate constants were found to be independent of initial pressure and, on increasing the surface/volume ratio by a factor of 10, the rate of reaction increased by approximately 20°/o. This increase in rate is ignored and the reaction declared "essentially independent of surface/volume ratio".

The only products reported are carbon dioxide and propene and the decomposition is said to take place by a purely molecular reaction. In the light of results obtained in studies of decompositions of other carboxylic acids it seems unlikely that the entire decomposition would take place by a purely molecular process without any part taking place by a radical process. No mention of analysis for hydrogen, $(C_3H_5)_2$, or carbon monoxide is made. Also

the authors mention no quantitative results of product analyses to facilitate the comparison of the numbers of moles of carbon dioxide and propene formed. These should be identical if the process is molecular.

On the other hand, the activation energy is low (39.3 kcal. $mole^{-1}$) and $D(C_3H_5 - COOH)$ would likely have a much greater value, arguing against the reaction

$$C_3H_5COOH \longrightarrow C_3H_5\cdot + \cdot COOH$$

The entropy of activation, ΔS^*, was calculated to be -10.2 cal. $deg.^{-1}$ $mole^{-1}$ at 650°K. This is good evidence for the cyclic transition state which Smith and Blan propose.

Phenylacetic Acid

The decomposition of phenylacetic acid has been studied by Back and Sehon using the toluene carrier technique[7] over the temperature range 587-722°C.

The main product of the decomposition was carbon dioxide, with smaller amounts of carbon monoxide. Hydrogen and methane were formed in amounts varying between 20 and 60°/o of the carbon dioxide, and the ratio of hydrogen to methane varied from 2 to 3.5. The yield of dibenzyl approached that of the non-condensable gases.

Back and Sehon were unable to account for all the acid decomposed from the total of carbon dioxide plus carbon monoxide formed. Phenylketen was also a product

of their reaction but even when allowance was made for this it was still impossible to completely account for the acid.

It was suggested that the decomposition takes place by two simultaneous routes:

$$C_6H_5CH_2COOH \longrightarrow C_6H_5CH_2\cdot + \cdot COOH$$

$$C_6H_5CH_2COOH \longrightarrow C_6H_5CHCO + H_2O$$

The rate constant for the former, the more predominant reaction, could be represented by

$$k = 8 \times 10^{12} \exp(-55{,}000/RT) \text{ sec.}^{-1}$$

The pre-exponential is within the limits for unimolecular reactions.

Increasing the surface/volume ratio by a factor of 27 caused the rate constant for the free radical dissociation reaction, above, to increase by only 30°/o. This indicated that this reaction was a homogeneous, first order process. The production of phenylketen was considerably increased in the packed reaction vessel and this mode of decomposition was thought to be partly heterogeneous. The percentage of carbon monoxide in the non-condensable gases also increased to about 50°/o although the total production of non-condensable gases was only slightly increased.

The identification of a strong acid, thought to be oxalic acid, in the products suggested that carboxyl radicals have a sufficiently long lifetime to react with

one another. If this can happen it is equally probable, if not more probable, that carboxyl radical could react with benzyl radical

$$C_6H_5CH_2\cdot + \cdot COOH \longrightarrow C_6H_5CH_3 + CO_2$$

Back and Sehon assign a ΔH of -63 kcal. mole^{-1} to this reaction.

Benzyl radicals are available from two sources in this reaction; from toluene, and from the acid itself. If toluene -d_8 or fully deuterated phenylacetic acid were used instead of one of the normally hydrogenated reactants it would be possible to ascertain whether reactions such as that above occur by studying the isotopic composition of the products.

Back and Sehon see the small amounts of dibenzyl formed relative to carbon dioxide as an indication of an alternative mode of decomposition of phenylacetic acid by a molecular rearrangement into carbon dioxide and toluene. However, they claim that the contribution of this reaction to the decomposition is relatively small on the basis that if it were a sizeable contributor the Arrhenius plot would not be linear as, in fact, it is, but would be a composite curve with contributions from the rate constants of the two decomposition processes.

Having made the assumption that recombination of radicals requires no activation energy, they identify the activation energy, 55 kcal. mole^{-1} with the bond

dissociation energy $D(C_6H_5CH_2 - COOH)$.

Diphenylacetic Acid

Back and Sehon[8] have also investigated the decomposition of diphenylacetic acid using the toluene carrier technique over the temperature range 515-636°C.

Carbon dioxide was the main product with carbon monoxide only a minor product. In this decomposition carbon monoxide accounted for about 35°/o of the non-condensable gases as compared to 10°/o in the decomposition of phenylacetic acid. They suggest that carbon monoxide and hydroxyl radical are formed from heterogeneous decomposition of carboxyl radical.

The decomposition was found to have an activation energy of 52 kcal. $mole^{-1}$ and a frequency factor of 8×10^{12} $sec.^{-1}$. The diphenylacetic acid decomposition appeared to be more affected by the surface conditions than was the decomposition of phenylacetic acid. Packing the reaction vessel to give a surface/volume ratio of 27 times that of the unpacked vessel greatly increased the overall decomposition and much larger quantities of what was thought to be diphenylketen were observed. The rate constant for the reaction

$$(C_6H_5)_2\ CHCOOH \longrightarrow (C_6H_5)_2\ CH. + .COOH$$

increased by a factor of three. Back and Sehon interpret

this threefold increase as an indication that only about 11°/o of the free radical decomposition occured on the surface of the reaction vessel, and consider the reaction to be primarily homogeneous.

They are hesitant to assign the activation energy to the dissociation energy of the $(C_6H_5)_2CH - COOH$ bond because of the uncertainty of the role of the surface in the decomposition.

Oxalic Acid

The decompositions of oxalic acid and oxalic acid $-d_2$ have been investigated by Lapidus, Barton, and Yankwich[9,10] at 0.9 mm and 127-157°C., and at 0.8 mm and 127-156°C., respectively.

In both cases the reaction was the same

$$\begin{matrix} (COOH)_2 \\ \text{or} \\ (COOD)_2 \end{matrix} \longrightarrow \begin{matrix} HCOOH \\ \text{or} \\ DCOOD \end{matrix} + CO_2$$

The formic acid products found in each case averaged 99.5 ± 0.5°/o of the carbon dioxide produced. Equivalence of the carbon dioxide produced and oxalic acid decomposed was also demonstrable to ± 1.0°/o.

The data were fairly reproducible indicating, perhaps, that no surface reaction took place. However, no surface effect studies were undertaken and no experiments

such as those with toluene -d_8 used in the present investigation of benzoic acid were carried out.

It is conceivable that this investigation of oxalic acid was carried out in its low pressure region and the kinetics could be quite different at higher pressures.[10]

For the non-deuterated acid the Arrhenius parameters were calculated and the rate constant could be represented as

$$k = 10^{12.7} \exp(-31{,}500/RT) \text{ sec.}^{-1}$$

The entropy of activation was -2.9 ± 2.1 cal. deg.$^{-1}$ mole^{-1}.[10]

For the deuterated acid

$$k = 10^{14.3} \exp(-34{,}500/RT) \text{ sec.}^{-1}$$

The entropy of activation was $+ 4.3 \pm 2.1$ cal. deg.$^{-1}$ mole^{-1}. These frequency factors indicate that the reactions are unimolecular. The values of the entropies of activation are taken as indicative of a cyclic transition state. The entropies are not very negative (the entropy change for the deuterated acid is, in fact, positive) which would suggest that if a cyclic transition state is operative, the cyclic species would be loosely bound together.

The first nine experiments in the reaction vessel exhibited a rate which was different from those experiments carried out after the vessel had been

conditioned by the repeated decomposition of oxalic acid.

In comparing the results obtained for the various carboxylic acid decompositions the great differences in them are obvious. Differences in stoiciometry, surface effects, effects of inhibitors and inert gases, and perhaps most important, the lack of a common mechanism to account for the greater part of any decomposition reaction, indicate the complexity of gas phase reactions of this type and their tremendous sensitivity to experimental conditions.

This investigation of the thermal decomposition of benzoic acid is a relatively new type of study, in that the decomposition reaction of the compound has not been previously studied in the gas phase. The present study has been undertaken to determine if it might be a gas phase elementary reaction and thus prove useful in isotope effect studies.

EXPERIMENTAL

I. Materials

(i) Benzoic Acid

"Fisher Primary Standard for Calorimetry" was used with and without further purification. The acid was melted and poured into a petrie dish. After cooling the cake was ground in an agate mortar,[11] placed on the vacuum line, evacuated at 0°C., melted, cooled, and reevacuated at 0°C. to remove water. A mass spectrum[12] indicated only benzoic acid using conditions for detection similar to those used for product analysis of fraction 4. (See later).

(ii) Toluene-d_8

Toluene-d_8 was obtained from Stohler Isotope Chemicals, Rutherford, New Jersey, catalog no. D 167, lot 3402, and was stated to be 99.5% D. It was used without further purification other than degassing which was carried out three times prior to each use.

(iii) Benzene

Fisher spectro-grade benzene was used without further purification.

(iv) Carbon Dioxide, Carbon Monoxide, and Hydrogen

All were obtained from Matheson and were used without further purification.

(v) Sodium Hydroxide

A solution was made up from a concentrated "Acculute" solution diluted with boiled, deionized water. The solution was usually standardized with benzoic acid.

II. Apparatus

(i) Infrared Spectrophotometer

All infrared spectra were recorded on a Perkin-Elmer 237B Grating Infrared Spectrophotometer using a pyrex gas cell with calcium fluoride windows and a 10 cm. pathlength.

(ii) Mass Spectrometer

Mass spectra were measured on a Consolidated Electrodynamics Corporation Residual Gas Analyser, 21-614, and were recorded by means of a Yokogawa Electric Works Ltd. Laboratory Recorder, LER-12A. See [12] also.

(iii) Vacuum System

The vacuum system was of the usual design. It consisted of six parts:

1. Sample introduction system.
2. Reaction vessel and pressure measuring system.
3. Temperature measuring apparatus.
4. System of cold traps for product separation.
5. Toepler pump and measured volume for product analysis.

6. Pumping system for evacuation of vacuum system.

These six parts are described below individually with reference to Fig. 1.

1. Sample introduction system

Acid was stored in a flask, 2. The air furnace, 7, was heated to approximately 170°C. and while in the air furnace the benzoic acid remained in the vapour phase. The reaction vessel was also connected, by means of a stopcock (A in Fig. 1.), to the air furnace contents.

The reservoir, 2, could be fitted with a small heater which was used to raise the temperature of the benzoic acid and hence increase its vapour pressure.

Extending from the side of the air furnace was a stopcock, F, to which could be attached a small flask, 1, volume 10ml., for the introduction of toluene-d_8 to the reaction vessel. The stopcock, F, was wound with heating tape and covered with wet asbestos and dried. This is shown as 11 in Fig. 1. It was maintained at a temperature of at least 130°C.

A heater, similar to that used around flask 2, could be placed around flask 1 to increase the toluene-d_8 vapour pressure. The temperature inside this heater was measured with a mercury thermometer.

2. Reaction vessel and pressure measuring system

The reaction vessel (Fig. 1, 5) was fabricated from a one litre spherical flask and is shown in Fig. 2. Prior to being blown into place on the vacuum line the interior surface of the reaction vessel was washed once with concentrated nitric acid, five times with ordinary tap-water and five with deionized water. This washing process was repeated once more. The reaction vessel was then blown into place on the vacuum line.

The pressure measuring system consisted of a pyrex Bourdon or "spoon" guage[13] (Fig. 1, 8), also shown in Fig. 3, and a mercury manometer (Fig. 1, 10). The manometer was connected to a vacuum pump (Fig. 1, 23) and to a vent whereby the pressure on the manometer could be varied by the removal or admission of air.

The Bourdon gauge was damped by Dow Corning 200 fluid (6 in Fig. 3), viscosity grade: 20 centistrokes at 25°C. The only problem encountered with this fluid was caused by the fact that the whole gauge assembly was located inside the air furnace (Fig. 1, 7) at approximately 170°C. The high temperature caused the oil to distill from the envelope (Fig. 1, 8) into the cooler parts of the system. This problem was rectified by the installation of the U-trap, at room temperature, (Fig. 1, 29), between the gauge and the rest of the system. The vapour condensed in the cooler U-trap and flowed back into the gauge.

Figure 3 shows the method whereby the spoon gauge was used in conjunction with two OCP 71 phototransisters (10), a lens (7), and an automobile headlight bulb (5).

The phototransistors were situated in an insulated, water-cooled box (Fig. 3, 9) equipped with a small glass window (8). The box was maintained at a temperature of 17 ± 2°C. during an experiment. A pressure differential from the spoon side of the gauge to the envelope side (Fig. 3, 1) caused the pointer (Fig. 3, 11) to move thereby moving the light beam, which passed through the glass ball (Fig. 3, 3), across the phototransistors and causing an imbalance in the phototransistor circuit (Fig. 4). This imbalance was displayed on a Leeds and Northrup Speedomax, type G, 10mV. recorder; zeroed down the centre of the chart paper. Imbalances were displayed as deflections of the recorder pen to the left or right of the centre position.

Pressure on the manometer was measured with a cathetometer which could be read to ± .001 cm. and the accuracy of the pressure measurement was ± .0125 cm.

The air furnace (Fig. 1, 7) was a large box, 26" x 22 1/2" x 17" (inside dimensions), made of asbestos board, and transite; a very hard, brittle and stone-like material with, it was found, only fair insulating properties. The furnace was fitted with three separate heaters; two of

which were controlled by Superior Electric Co. "Powerstats" and which were operating continuously. The third was connected to a Precision Scientific Electronic Relay; Catalog no. 62690, which was controlled by an American Instrument Co. "Quickset" 4-239 bimetallic regulater. The temperature was held constant in this manner to better than $\pm$ .5°C. during an experiment.

The heated air was circulated by a Fisher Scientific Fultork Labmotor to which was attached a fan approximately four inches in diameter. However, the agitation of the heated air by the fan was not sufficient to provide a uniform temperature throughout the box. The temperature varied from a low of approximately 170°C. to a high of approximately 200°C. as measured by five mercury thermometers distributed throughout the air furnace.

The air furnace was fitted with a light to illuminate the interior, a window through which the contents could be viewed, and remote controls for the operation of most of the stopcocks inside. Figure 5 shows one of the remote controls.

At the rear of the air furnace was a door which could be removed so that two small stopcocks (Fig. 1, G and H) could be operated by means of a piece of lightweight pipe one end of which was equipped with notches which could be fitted around the stopcock handle and the handle turned.

The remote controls in Figure 5 are rods fitted

with a handle at one end and a device which was fitted over the stopcock handle on the other. The front of the air furnace was fitted with bushings so that the remote controls would be well supported and could turn freely.

The reaction vessel was surrounded by a large high-temperature furnace which could be raised or lowered on a scissors-type jack. See Figure 6. The furnace consisted of a steel cylinder wrapped with asbestos and with several heaters around it. The cylinder was equipped with a top in which there was a slot to enable the top to be slipped on or off when the neck of the reaction vessel was protruding out of the top of the furnace. When the top was in place a piece of steel was inserted in the slot.

Six separate heaters were wound around the steel cylinder. They were made from 20 gauge chromel-A wire (.642 ohm/ft.) from Hoskins Alloys Canada Ltd. The heaters were arranged in two layers of three heaters each. The leads from the heaters were electrically insulated with small pieces of pyrex tubing which were slipped over them individually until each lead was completely covered. This method gave good electrical insulation and retained flexibility. The leads were then attached to terminals on a panel at the front of the furnace. (See figure 6).

The reaction vessel neck, between the vessel and the air furnace, 5 inches, was wound with 28 gauge

chromel-A heater wire insulated with asbestos (Fig. 1, 11). Power for the heater was supplied through and regulated by a Sunvic type E.R.C. Energy Regulater. The temperature was controlled to $\pm$ 3°C. and was maintained in the range 418-425°C.

The furnace was raised until it came into contact with the above-mentioned reaction vessel neck winding. As can be seen from Figure 6 the furnace was enclosed in an asbestos board outer jacket which extended from the table-top to within eight inches of the bottom of the air furnace.

Power for all the furnace heaters but one was supplied by Superior Electric Co. Powerstats. The sixth was the middle heater in the outer layer of heaters and was connected to a Hallikainen Instruments Resistotrol which was connected directly to the mains. The Resistotrol was regulated by a platinum resistance thermometer, also supplied by Hallikainen, which occupied one arm of a bridge circuit. Furnace temperature was maintained to $\pm$ .1°C. The platinum resistence thermometer's position with respect to the furnace and reaction vessel is shown in Figure 6.

3. Temperature measuring apparatus

The method of using thermocouples for temperature measurement was employed. The thermocouples were of the chromel-alumel type. Four thermocouples were used for reaction vessel temperature measurement. One thermocouple

was at the top of the reaction vessel, one at the bottom, one at the inner end of the thermocouple well, and the fourth was halfway in the thermocouple well. A fifth thermocouple was also placed in the reactor neck winding below the air furnace (Fig. 1, 11).

The four thermocouples used in and around the reaction vessel were calibrated with the freezing points of lead, zinc, and tin. The metals were U.S. Dept. of Commerce, National Bureau of Standards, standard samples and had freezing points of 327.417°, 419.50°, and 231.88°C. respectively. The two thermocouples used in the well were the two which were in closest agreement with the given value for zinc since its freezing point is closest to the temperatures used in this study; i.e. numbers 1 and 4, Table I.

Table I lists the results obtained on calibration of the thermocouples:-

TABLE I

Thermocouple No.	1	2	3	4
Freezing Pt. of Std. (°C)	327.417	327.417	327.417	327.417
Observed Freezing Pt. (°C)	326.98	326.92	327.32	326.96
Deviation (°C)	-.44	-.50	-.10	-.46
Freezing Pt. of Std. (°C)	419.50	419.50	419.50	419.50
Observed Freezing Pt. (°C)	417.57	419.90	420.01	419.47
Deviation (°C)	+.07	+.40	+.51	-.03
Freezing Pt. of Std. (°C)	231.88	231.88	231.88	231.88
Observed Freezing Pt. (°C)	232.36	232.58	232.56	231.36
Deviation (°C)	+.48	+ .70	+.68	-.52

The places where thermocouple wire was soldered to copper wire, for both hot and cold junctions, were all taped together so that they would all be at the same temperature and hence there would be no difference in potential.

The cold junction was enclosed in a long glass tube which was immersed in a two-quart dewar flask containing a slush of chipped ice and deionized water. The ice was produced by a laboratory ice-making machine from tap-water. The slush was stirred intermittently while temperature

readings were being taken so that the temperature remained uniform throughout.

Thermocouple emfs. were measured on a Doran D.C. Potentiometer from Derritron Instruments Ltd., catalog no. E4248. Emfs. could be measured to ± .002 millivolts. A Minneapolis Honeywell Rubicon Instruments galvanometer, catalog no. 3433-3, was used for balancing the potentiometer. Power for balancing the circuit was supplied by a two volt tap from a six volt automotive battery. The battery required charging every two or three months. The need for recharging was easily recognized since it became impossible to standardize or balance the potentiometer.

At one stage in the work it became necessary to replace the internal standard cell in the potentiometer with an Epply Laboratory standard cell, catalog no. 100, internal resistence less than five hundred ohms, and emf. 1.0186 volts.

4. System of traps for product separation

These are shown in Fig. 1 as numbers 12, 25, 26, 27, and 28. The main trap is 12. As can be seen from Fig. 1, the glass tubing to and from the "U" was heated (11). 25 is a removable finger used for the removal of compounds which were solids at room temperature and atmospheric pressure.

The temperature of the U-trap winding, 11, was measured in three places where thermocouples were positioned.

Temperature readings could be taken at points near either end of the winding and also on the barrel of the stopcock on the right hand side of the winding. The temperature at the air furnace end of the winding was approximately 240 $\pm 2^{\circ}C$. during an experiment and at the stopcock end it was 140 $\pm 2^{\circ}C$. The temperature was controlled by a type E.R.C. energy regulater from Sunvic Controls Ltd.

Trap 27 was used mainly for condensing carbon dioxide in the process of separating it from other products.

The copper oxide furnace (Fig. 1, 13) was a pyrex tube containing small pieces of oxidized copper wire supplied by Fisher Scientific. The heater surrounding the copper oxide was controlled in the same way as was the U-trap winding, 11. A thermocouple was embedded in the insulation against the pyrex tubing of the furnace.

The cold baths were contained in dewar flasks which could be fitted around the U-trap (Fig. 1, 12) until the coolant was almost in contact with the windings, 11.

Coolants used and their approximate temperatures were:[14]

Liquid Nitrogen	$-196^{\circ}C$
Ethanol Slush	$-116^{\circ}C$
Isopropanol/Dry Ice	$-78^{\circ}C$
Chlorobenzene Slush	$-45^{\circ}C$
Water/Ice	$0^{\circ}C$

5. Toepler pump and measured volume

The toepler pump and measured volume are shown in Fig. 7 and in Fig. 1; 14 and 16, respectively.

The toepler pump was constructed for automatic operation, being set up in such a way that it could collect or cycle gases while unattended. The pump was equipped with a float valve; Fig. 1, 15, which was surrounded by an induction coil wound on the pyrex tubing. When the mercury in the pump activated the automatic relay it also activated the induction coil which forced the float valve down making a gas-tight seal; trapping some mercury above it.

As can be seen in Fig. 1, the measured volume, 16, consisted of two parts. The main part was the volume between the mercury surface in the left arm of the manometer and a mark above float valve 15. The manometer was made from standard wall, 15 m.m. O.D. pyrex tubing.

Calibration of the measured volume was achieved by filling a bulb of known volume with an atmosphere of carbon dioxide and attaching this to the vacuum line. The bulb was then opened to the manometer, 16, and the pressure of carbon dioxide measured. The bulb was then closed off and the carbon dioxide between it and the manometer was pumped off. The contents of the bulb were then toepler pumped to the manometric section of 16 and the pressure of carbon dioxide on the manometer was measured

for a large number of positions of the mercury meniscus. From these readings a graph of volume versus position of mercury meniscus could be plotted and hence the volume of the tube calibrated throughout its length.

Pressure and position of meniscus readings on the measured volume manometer were made using a Gaertner Scientific Corp. cathetometer readable to ± .005 cm. The position of meniscus readings was determined by noting, through the cathetometer, the height of the left arm of mercury relative to a meter stick attached to the manometer.

The stopcock below the bulb, 16, was a three-way stopcock. One arm was fitted with a standard-taper joint for the removal, in tubes, of samples from the manometer measured volume for spectral analysis. Each time the measured volume was used the mercury in the toepler pump was raised to the same position as it had been when the volume of 16 was calibrated.

6. Pumping system for evacuation of vacuum system

The pumping system was equipped with a Welch Scientific Co. Duo-Seal forepump, Fig. 1, 20, connected in series with a Balzers Diff 10W oil diffusion pump, 19, which could be by-passed and the system evacuated with only the forepump if desired.

A large ring-seal trap, 18, maintained at -196°C by immersion in liquid nitrogen, was situated between the pumps and the rest of the vacuum line.

For pressure measurement a Consolidated Vacuum Corp. thermocouple vacuum gauge, type GTC-100, with two separate sensors, was used. The location of these sensors is indicated in Fig. 1 at 3 and 4. 4 made it possible to determine when toepler pumping was completed. Pressures could be measured down to about 1×10^{-3} m.m. in this manner.

For measurement of lower pressures a Kontes Glass Co., Model E, McLeod gauge was fitted. It was possible to read pressures as low as 1×10^{-6} m.m. The McLeod gauge is shown in Fig. 1, 21.

To ensure accurate pressure readings with the McLeod gauge the outlet from the main pumps was closed and the pressure throughout the system allowed to equilibrate. Ten to fifteen minutes was found to be sufficient time to accomplish this.

For analysis of unreacted benzoic acid a titration procedure, to be described later, was used. The buret used in the analysis was a 10 ml. "A" grade buret with teflon plug which could be read to $\pm$ .005 ml. A 25 ml. "A" grade pipet was also used. Both the buret and pipet were made by Kimax. All solutions were made in "A" grade volumetric flasks.

All experiments were timed using either a Labchron 1400 or 1401 timer from Labline Instruments. The model 1400 was graduated in seconds and could be read to the nearest one tenth of a second. The model 1401 was graduated

in minutes and could be read to the nearest one hundredth of a minute. The latter was used for the longer experiments.

III. Procedure

(1) Sample Introduction

Prior to sample introduction the benzoic acid storage bulb (Fig. 1, 2) was pumped until the pressure therein reached a sufficiently low value (approximately 10^{-5}mm. Hg.) while being held at 0°C. When the pressure reached 10^{-5} m.m. of Hg, stopcock E was closed and the ice/water slush bath replaced by a small heater. The acid was heated to 120-150°C, depending on the starting pressure desired.

Stopcocks A, B, C, F, and G were closed. Stopcock E was opened and the acid allowed to evaporate from 2 into the five-litre bulb, 24. The increasing pressure of acid was followed and measured, as described below, with the spoon gauge (Fig. 1, 8; Fig. 3) and when the pressure in 24 had reached the desired level stopcock E was closed and the acid heater turned off.

Stopcock A was now opened and the acid admitted to the reactor. The clock was started as soon as A was opened. Five seconds after opening, A was closed again and the starting pressure measured, the benzoic acid pressure in 24 now being the same as that in 5 at the start of the reaction.

Thermocouple readings were made immediately after the reaction vessel was filled and the starting pressure measured. Acid which was not put into the reaction vessel, 5, was distilled back into 2.

(2) "Conditioned" and "Unconditioned" experiments

It was impossible to obtain reproducible rates of reaction by merely filling the reaction vessel as described above, and allowing the reaction to proceed. Reactions carried out in this manner will be referred to as "unconditioned".

The rate of reaction was found to be reproducible to $\pm$ 5°/o by using the following procedure: The acid was introduced to the reaction vessel in the previously described manner and the reaction was allowed to procede for 600 sec. at 498.5°C., for 2000 sec. at 486.0°C., and for 3000 sec. at 475.1°C. after which time the reaction vessel was emptied and the vessel immediately refilled. The starting pressure was measured as usual. Reactions carried out in this manner were studied using varying reaction durations and initial concentrations of acid.

(3) Pressure measurement

Pressure measurements were carried out by leaking air into or pumping it out of the envelope side of the spoon gauge (Fig. 3, 1) until the pen on the recorder moved to the zero position, i.e., the centre of the chart paper. At this time the pressure on the envelope side,

1, was equivalent to that inside the spoon, 2, and hence equal to the pressure in the tubes contained in the air furnace (See Fig.1, 8).

The pressure of the envelope side was displayed on the mercury manometer (Fig.1,10) and measured with a catheto-meter which could be read to $\pm$ .001 cm. The pressure of benzoic acid could be read to $\pm$ .0125 cm.

(4) Analysis

The materials removed from the reaction vessel following an experiment could be divided into four categories (See also pp.44-45).

1. That which passed through a -196°C trap.
2. That which was trapped by -196°C but passed through -116°C.
3. That which was trapped by -116°C but passed through -45°C.
4. All that remained after removal of the above three fractions.

The first fraction was toepler pumped to the measured volume (Fig.1,16) and then removed and analysed by mass spectrometry. The second fraction was treated in the same manner as the first. Gases could be analysed to better than $\pm$ 3 %.

The third fraction, which was composed of sub-stances which were liquids at room temperature and atmospheric pressure (e.g. benzene), was distilled into a gas cell (previously described) and its infrared spectrum recorded.

Benzene could be analysed both qualitatively and quantitatively in this way.

A plot of absorbance vs. number of moles of benzene was made from results obtained from filling the gas cell with spectrograde benzene. Filling the cell with a microlitre syringe or by evaporating it into the reaction vessel at known pressure, temperature, and volume and then distilling the benzene into the cell gave similar results averaging $\pm$ .02 x 10^{-3} moles from the straight line shown or 5°/o for the largest sample analysed and 30°/o for the smallest (See Fig. 9, Table VI, and Table II).

Fig. 8 shows a sample infrared spectrum of the third fraction and spectrum of spectrograde benzene. The band at 1820 cm^{-1}. was used for quantitative analysis.

The fourth fraction was removed by heating and distilling from 12 to 25 in Fig. 1. Quantitative analysis for unreacted benzoic acid was then carried out. Qualitative analysis was carried out once by means of mass spectrometry.[12] The results of this mass spectrum are listed in the "Results" section, Table V.

Unreacted benzoic acid was quantitatively analysed by titration of a deionized water/neutralized ethanol solution[11] of the acid with .100 N. sodium hydroxide solution (carbonate free). The ethanol was neutralized to the phenolphthalein end point by the addition of sodium hydroxide. Phenolphthalein was also used as the indicator

TABLE II

Infrared calibration for benzene analysis

	No. of moles C_6H_6 in cell	Absorbance
	$.338 \times 10^{-3}$	.143
	$.450 \times 10^{-3}$	.209
	$.338 \times 10^{-3}$	.167
	$.169 \times 10^{-3}$	.089
*	$.442 \times 10^{-3}$	.212
*	$.376 \times 10^{-3}$	.200
	$.338 \times 10^{-3}$	.171
	$.141 \times 10^{-3}$	.087

* Cell filled by pressure measurement.
All others cell was filled with microliter syringe.

in the titration of the unreacted acid. The unreacted acid was dissolved in the neutralized ethanol while still contained in 25, Fig. 1, and poured into a 100 ml. "A" grade volumetric flask and then made up to the mark with deionized water. Three 25 ml. aliquots of this solution were titrated with the .100 N. sodium hydroxide solution.

TABLE III

Test of titration method of benzoic acid analysis

moles acid weighed out $\times 10^3$	moles titrated $\times 10^3$	% difference
.748	.736	1.71
.432	.438	1.37
.601	.610	1.50
.777	.773	.57

(5) Sample introduction in experiments with toluene-d_8 present

Prior to commencing an experiment the toluene-d_8 was weighed in its reservoir (Fig. 1, 1) and then degassed three times. The reservoir, 1, was then heated to approximately 115°C with a heater identical to that used for heating the benzoic acid contained in 2. The area between 1 and the air furnace, 11, was also heated to

approximately the same temperature. Both 1 and 11 were heated for at least one hour before beginning a reaction.

The benzoic acid was introduced into the reaction vessel in the same manner as described previously, the five-litre bulb, 24, being emptied of acid by pumping through the U-trap, 12, for five minutes. The toluene-d_8 was allowed to evaporate, to fill the bulb, 24, for periods ranging from two to six minutes. Stopcock A was opened for from five to ten seconds and the toluene-d_8 allowed to enter the reaction vessel. Stopcock A was then closed and the toluene-d_8 distilled back into its reservoir, 1, for at least five minutes. The toluene-d_8 and 1 were weighed and the quantity of toluene-d_8 in the reaction vessel was calculated.

In the experiments involving toluene-d_8, only the pressure of acid in the five-litre bulb, 24, was measured. As can be seen in Table IV, below, the starting pressure can be accurately calculated when the pressure of the acid in 24 is known.

Ratio of Air Furnace Pressure to Starting Pressure

Reactor Temp. 498.5°C

Run Number	Air Furnace Pressure/Starting Pressure	
112	1.108	
110	1.108	
109	1.102	
108	1.114	
116	1.099	
117	1.107	
118	1.116	
119	1.107	
120	1.106	
121	1.109	Average Value 1.108

Toluene-d_8 was used as a source of deuterium.[15] If phenyl radicals were present they might abstract deuterium from toluene-d_8; C_6H_5D (m/e 79) could be distinguished from C_6H_6(m/e 78) by mass spectrometry. In experiments with toluene-d_8 the m/e ratio 79/78, corrected for contributions to the 78 -peakffrom the fragmentation of toluene-d_8 and to the 79 peak from the (primarily C^{13}) isotope peak of C_6H_6, was taken as a measure of the C_6H_5D/C_6H_6 molar ratio. The corrections were made by comparisons with mass spectra of pure toluene-d_8 and of spectrograde benzene, respectively.

(6) Sample introduction in experiments with air present

Air was leaked into the reaction vessel through the stopcock at 26 (Fig.1) whereby it passed through the U-trap, 12, which was held at -196°C. to freeze out any vapour present. The pressure of the air in the system was measured with the McLeod gauge, 21, (Fig.1) and

then stopcock A was closed and all the air which had been leaked into the system was pumped out except that contained in the reaction vessel. Benzoic acid was then introduced in the manner described previously.

The purpose of these experiments was to determine the effect of the reaction rate of a leak into the reaction vessel. This was thought necessary because (a) the stopcocks in the air furnace were maintained at a high temperature (approximately 170°C.) which caused the lubricating Dow Corning Silicone grease to become less viscous and possibly leak and (b) it was thought that the irreproducibility of the reaction rate might be caused by the presence of a small and variable pressure of oxygen.

RESULTS

I Products

The main products in the reaction are carbon dioxide, carbon monoxide, benzene, and biphenyl. Table V, below, lists the products found and suggested[12] from an experiment carried out at 475.1°C. (Prior to this experiment the reaction vessel was pumped overnight). The reaction duration was 50.67 hours.

TABLE V

Products from a Reaction at 475.1°C as found by Mass Spectrum[12].

Note: The fractions are as defined in the "Experimental Section" (See p.36), except that a 0°C trap was used instead of a -45° trap for fraction 3.

Fraction	Product	% of Sample
1.	CO	92.65
	CH_4	5.02
	O_2	2.33
2.	CO_2	100.
3.	Sample was mainly benzene. The presence of phenol was also indicated but its vapour pressure, which is relatively low at room temperature, might prevent its being observed in its true proportion.	

relative to benzene. This fraction also contained silicone compounds from silicone oil and grease in the system.

After evaporating off the benzene the sample was rescanned and biphenyl was then detected. The m/e 46 peak (M.W. formic acid = 46) was very small in both spectra.

Fraction 4. The following assignments were suggested for mass numbers identified:

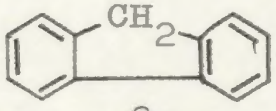
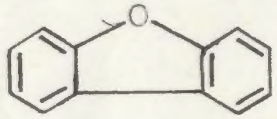
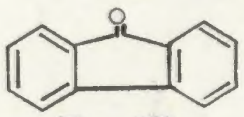
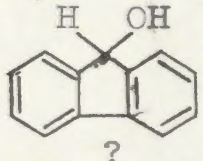
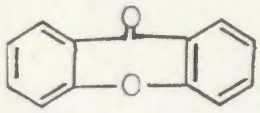
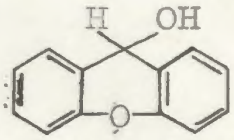
m/e	compound suggested *
94	phenol
122	benzoic acid
154	biphenyl
166	
168	
170	diphenyl ether or hydroxybiphenyl
178	anthracene
180	
182	
192	?
194	?

Table V (con'td.)

m/e	compound suggested*
196	
198	
230	triphenyl.

*All compounds except the first three of this table are present in very small amounts.

It was suggested that isobaric compounds should not be ignored. This is perhaps a wise warning because the oxygen linked ring compounds seem somewhat unlikely unless they are present as impurities in the acid when it is put in the reaction vessel. A mass spectrum of the benzoic acid used[12] showed no impurities present.

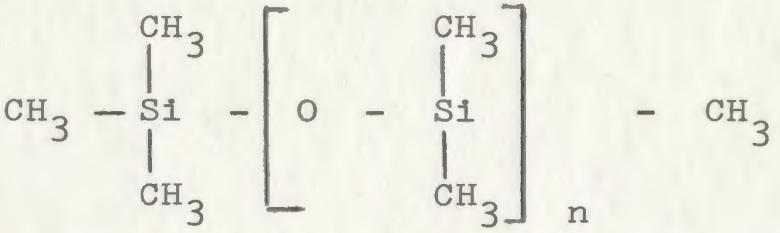
Mass spectral analyses[16] indicated that traces of hydrogen were present in the decomposition products.

No quantitative analysis for phenol or biphenyl was carried out.

The experiment from which the data for Table V were obtained was carried out in an unconditioned reaction vessel. Mass spectra of fraction 3 for conditioned experiments[16] did not contain any m/e 46. The fact that m/e 46 is mentioned in Table V but was not found for conditioned experiments is not necessarily a contradiction since the stoichiometry of reactions carried out under each of these

conditions was slightly different.

Methane was found on only a very few occasions. One possible explanation for the presence of methane, proposed by Dow Corning Silicones Ltd.,[17] is that methyl groups could be produced from decomposition of the silicone grease used on the air furnace stopcocks and also from the Dow Corning 200 fluid which was used to damp the vibrations of the spoon gauge. They give the following general structure for both fluid and grease



The bond energies of Si-C are of the order to 69-76 Kcal. mole while the energy of the Si-O bond is 88-108 Kcal./mole. On prolonged heating at 200°C it seems reasonable that the Si-C bond will break preferentially yielding a methyl group.[17]

The sum of the carbon monoxide and carbon dioxide produced and the undecomposed acid recovered accounted for 92-98% of the initial amount of acid in most conditioned experiments. (See Table VI). There is a slight correlation between percentage of acid missing and reaction time; the percentage decreases from an experiment of 2000 sec. duration through 9000 sec. to 16000 sec. but data are not sufficient to state this with certainty. Experiment 93, (Table VI, p.49 with 20.06% acid missing, is certainly not consistent

with the other data. In Table VI, p.49, experiments 93, 97, 102, 110, 112, 116 and 127 have the same starting pressure of benzoic acid. All the experiments listed on p.49 were carried out at 498.5°C.

The best carboxyl group balances were obtained both early and late in the reactions but never in the 50% extent of reaction region.

In Table VI where no benzoic acid titrations were carried out the % reaction was calculated from the carbon dioxide and carbon monoxide produced relative to the quantity of acid introduced into the reaction vessel i.e. $\frac{CO + CO_2}{(C_6H_5COOH)_{t=o}} \times 100$. It assumes no other products from COOH except carbon monoxide and carbon dioxide.

As can be seen in Table VI the ratio $\frac{CO}{CO + CO_2}$ (or $\frac{CO + H_2}{CO + CO_2 + H_2}$) in unconditioned experiments is lower than that for similar conditioned experiments.

From Table VI the quantity of benzene produced is always less than the quantity of carbon dioxide. This may truly represent what is taking place, or some of the benzene may have been absorbed by the grease in the system and on the infrared cell stopcocks. It is difficult to determine how much of the benzene would be absorbed by the grease and hence not contribute to the spectrum.

TABLE VI

Product Analyses *

Part I Temp. 498.5°C Reaction Vessel Conditioned.

Run	moles acid in x 10^3	moles acid out x 10^3	moles acid reacted x 10^3	CO_2 moles x 10^6	C_6H_6 moles x 10^6	CO moles x 10^6	H_2 moles x 10^6	% acid unaccounted for	$\frac{CO}{CO + CO_2}$ %	Reaction Time sec.	% Reaction
93	.717	.488	.229	142.6	137.0	40.79	.12	20.08	22.28	10,500	31.95≠
97	.769			28.64		10.82	.11		27.40	2,600	5.14
102	.756			513.0		32.80	1.18		6.02	12,000	72.25
110	.808	.034	.774	649.1	510.0	102.4	1.53	2.69	13.62	17.3 hrs	95.80≠
112	.768	.676	.092	27.32		6.95	.06	7.80	20.25	2,000	4.52≠
116	.792	.566	.226	138.7	121.0	29.90	.30	7.27	17.70	9,000	28.55≠
127	.783	.415	.368	249.4	210.0	76.78	.45	5.26	23.50	16,000	41.68≠
151	.229	.123	.106	76.64	66.3	10.22	.08	8.37	11.77	16,000	37.88≠

≠ from titration of benzoic acid.

* See addendum at end of thesis for % reactions.

Table VI (cont'd)

Part 2 Temp. 475.1°C. Reaction Vessel Unconditioned

Run	moles acid in x 10^3	moles acid out x 10^3	moles acid reacted x 10^3	CO_2 moles x 10^6	C_6H_6 moles x 10^6	$(CO + H_2)$ non-cond. moles x 10^6	°/o acid unaccounted for	$\frac{CO + H_2}{CO + CO_2 + H_2}$ °/o	Reaction Time Sec.	°/o Reaction
36	.546			451.0		45.50		9.15	50.67 hrs.	90.90
33	.341			1.23		.135		9.90	315	.401
32	.229			.817		.052		5.98	315	.38
31	.311			2.27		.083		3.53	315	.76
30	.524			1.76		.203		10.33	315	3.75
29	.232			.469		.0997		17.5	315	.25
21	.252	.016	.236	213.0	208.0	9.79	5.17	4.48	21.6 hrs	88.50*
20	.133	.008	.125	115.0	109.0	2.86	5.65	2.54	19.5 hrs	88.70*
19	.459			474.0	415.0	15.1		3.07	20.5 hrs	
18	.377	.016	.361	366.0		18.3		4.77	17.2 hrs	
37	.299			7.38		.758		9.34	3,000	2.72
38	.304			4.07		.344		7.72	3,000	1.45
39	.327			3.90		.350		8.24	3,000	1.30
40	.327			3.63		.314		7.87	3,000	1.21
41	.317			3.80		.392		9.31	3,000	1.32
42	.765			8.32		1.04		11.11	3,000	1.22
43	.388			3.53		.334		8.55	3,000	.996
45	.355			6.36		1.58		19.82	3,000	2.24
46	.331			3.20		.610		16.00	3,000	1.41
47	.326			2.39		.472		16.43	3,000	.88
48	.330			3.15		.599		16.00	3,000	1.14
49	.349			3.04					3,000	

Note: In experiments where no titration was carried out to determine the number of moles of acid unreacted, °/o reaction was calculated from the equation: $\frac{CO + CO_2}{\text{(reactants total)}} \times 100$
It assumes no other product from -CCOH except CO and CO_2

II Conditioning of Reaction Vessel

Conditioning the reaction vessel, as described in the "Experimental" section, was carried out at least once prior to each experiment and, in cases where the reaction vessel had been opened to the atmosphere (e.g. during re-greasing), it was necessary to condition the reaction vessel with five or six experiments. Each successive conditioning experiment reduced the rate of reaction until the results exhibited considerable scatter. (See Fig.14, e.g. Note scattering in range $Log_{10}C_{BA} = 3.2$, C_{BA} = concentration of benzoic acid in moles litre^{-1}). The problem of scattering of results was greatly increased by venting the reaction vessel to the atmosphere. (See Fig.20).

The effect of conditioning the reaction vessel on the rate of reaction is evident from Fig.13; the pressure-time curves of conditioned and unconditioned experiments and also from Fig.20.

Since the spoon gauge was not connected directly into the reaction vessel, it was necessary to carry out the experiments from which Fig.13 is derived with stopcocks A and H, Fig.1, open. Stopcocks B, C, D, E, F, and G were closed. The effect of carrying out the experiments in this manner was to increase the "dead-space" of the reaction vessel by about 125 cc. This produced a dead-space of about 12 % of the reaction vessel volume. Correctio-s for the effect of dead-space on the reaction[18] have not been carried out.

Table VI shows the non-reproducibility of unconditioned experiments.

III Initial Rates

Experiments were carried out at 475.1, 486.0, 498.5°C. and the results obtained for carbon dioxide formation are shown in Table VII, for carbon monoxide formation in Table VIII, for hydrogen formation in Table IX, and for (carbon dioxide + carbon monoxide) formation in Table X. The data given in these tables are represented graphically in Figs. 14 to 17.

It can be seen from Figs. 14 to 17 that the order for the formation of hydrogen is higher than that for carbon dioxide according to the preliminary data. The order for the formation of carbon monoxide (approximately 2) is also higher than that for carbon dioxide. The order of thereaction from the carbon dioxide data has been calculated[19] by a method of least squares (Table XI).

TABLE XI

Order for CO_2 formation

Temp(°C)	log k	k x 10^5	order
475.1	-4.9833 ± .0079	1.040 ± .002 (.20 −.20) l. m. s.$^{-1}$	1.1985 ± .0276
498.5	-4.1508 ± .0123	7.066 ± .021 (.30 −.30) l. m. s.$^{-1}$	1.2766 ± .0418

However, the hydrogen and carbon monoxide results are strictly preliminary.

It is worth noting that there is a small divergence in slope, and hence in the order, shown for the two curves in Fig. 14. This divergence will greatly exaggerate the difference in rate constants at the intercept and hence calculation of the activation energy, E, using $\Delta \log k$ would give a misleading value. The activation energy was calculated using the assumption that the rate expression is of the form (n being the same at all temperatures)

$$\text{Rate} = k\,[\text{B.A.}]^{n}$$

Calculating from the data obtained from the centre of the $\log_{10} C_{BA}$ axis in Fig. 14, E was found to have a value of 62,200 cal. mole^{-1}. Log A, where A is the Arrhenius pre-exponential or frequency factor, was found to be 13.41. Units for A are $\text{l.}^{.25}\ \text{mole}^{-.25}\ \text{sec.}^{-1}$.

Similarly, calculating for the left-hand end of the $\log_{10} C_{BA}$ axis in Fig. 14 the following values are obtained:

$$E = 57{,}300 \text{ cal. mole.}^{-1}$$

$$\log A = 11.99$$

and for the right-hand end the corresponding values are:

$$E = 66{,}280 \text{ cal. mole.}^{-1}$$

$$\log A = 14.57$$

TABLE VII

Initial Rate of Formation of Carbon Dioxide

Temp. 498.5°C., Reactor Volume 1.162 l.

Run	Starting Pressure (cm.)	moles acid in $\times 10^3$	moles per litre $C_{BA} \times 10^3$	moles CO_2 produced $\times 10^6$	CO_2 moles/litre $\times 10^6$	Reaction Time (Sec.)	Rate CO_2 moles/litre/sec. $\times 10^9$	$\log_{10} C_{BA}$	$\log_{10}$ Rate CO_2
84	1.304	.3137	.2700	1.48	1.27	600	2.11	-3.5686	-8.6757
85	1.338	.3221	.2772	2.96	2.55	1200	2.13	-3.5572	-8.6716
87	1.784	.4291	.3693	1.58	1.36	600	2.27	-3.4326	-8.6440
88	1.777	.4275	.3679	1.65	1.42	600	2.37	-3.4342	-8.6253
89	3.038	.7308	.6289	2.66	2.29	600	3.82	-3.2014	-8.4179
90	0.749	.1802	.1551	0.624	0.537	600	0.895	-3.8094	-9.0482
92	2.835	.6833	.5880	2.51	2.16	600	3.60	-3.2306	-8.4437
95	3.395	.8186	.7045	13.38	11.52	1500	7.68	-3.1521	-8.1146
99	3.158	.7611	.6550	3.33	2.87	600	4.78	-3.1838	-8.3206
106	0.958	.2310	.1987	1.39	1.20	600	2.00	-3.7017	-8.6990
107	0.990	.2388	.2055	1.16	0.998	600	1.66	-3.6871	-8.7799
108	0.895	.2160	.1859	0.987	0.849	600	1.42	-3.7307	-8.8477
109	0.952	.2298	.1978	0.945	0.813	600	1.36	-3.7037	-8.8665
115	3.155	.7611	.6550	3.14	2.70	600	4.50	-3.1838	-8.3468
122	3.309	.7982	.6869	5.32	4.58	600	7.63	-3.1631	-8.1175
123	3.328	.8028	.6909	5.26	4.53	600	7.55	-3.1606	-8.1221
124	3.412	.8238	.7090	5.23	4.50	600	7.50	-3.1494	-8.1249
131	3.301	.7970	.6859	6.72	5.78	600	9.63	-3.1638	-8.0164
133	3.348	.8079	.6953	4.36	3.75	600	6.25	-3.1578	-8.2041
136	3.313	.7996	.6881	2.30	1.98	600	3.30	-3.1623	-8.4815
138	2.086	.5038	.4336	1.61	1.39	600	2.32	-3.2977	-8.6345
142	3.435	.8301	.7144	6.65	5.72	600	9.53	-3.1461	-8.0209
143	3.416	.8243	.7094	5.74	4.94	600	8.23	-3.1492	-8.0846

Table VII contd.

Run	Starting Pressure (cm.)	moles acid in $\times 10^3$	moles per litre $C_{BA} \times 10^3$	moles CO_2 produced $\times 10^6$	CO_2 moles/litre $\times 10^6$	Reaction Time (Sec.)	Rate CO_2 moles/litre/sec. $\times 10^9$	$\log_{10} C_{BA}$	$\log_{10}$ Rate CO_2
144	1.500	.3621	.3116	2.41	2.07	600	3.45	-3.5064	-8.4622
145	0.980	.2366	.2036	1.12	0.964	600	1.61	-3.6912	-8.7932
146	0.979	.2364	.2034	1.07	0.922	600	1.54	-3.6917	-8.8125
149	1.602	.3869	.3330	3.55	3.06	1000	3.06	-3.4776	-8.5143
150	1.630	.3937	.3388	3.11	2.68	1000	2.68	-3.4701	-8.5719
Temp. 486.0°C., Reactor Volume 1.162 l.									
158	3.232	.7929	.6824	8.16	7.02	2000	3.51	-3.1659	-8.4547
159	1.198	.2939	.2529	1.78	1.53	2000	0.765	-3.5971	-9.1163
160	2.443	.5993	.5157	5.13	4.42	2000	2.21	-3.2876	-8.6556
Temp. 475.1°C.				* experiment carried out in presence of air					
50	1.371	.342	.294	1.91	1.64	3000	0.55	-3.5317	-9.2596
51	1.377	.343	.295	2.02	1.74	3000	0.58	-3.5302	-9.2366
53	1.401	.349	.300	2.19	1.89	3000	0.63	-3.5229	-9.2007
54	2.021	.503	.433	3.44	2.96	3000	0.99	-3.3635	-9.0044
55	2.901	.722	.621	4.91	4.23	3000	1.41	-3.2069	-8.8508
57	0.520	.129	.111	.503	.433	3000	.144	-3.9547	-9.8416
58	4.046	1.007	.867	5.74	4.94	3000	1.65	-3.0620	-8.7825
59	2.500	.622	.535	4.31	3.71	3000	1.24	-3.2716	-8.9066
62	0.793	.197	.170	1.56	1.34	3000	0.45	-3.7696	-9.3468
63	0;784	.195	.168	1.39	1.20	3000	0.40	-3.7747	-9.3979
64	0.935	.233	.201	1.62	1.39	3000	0.46	-3.6968	-9.3372
65	0.885	.220	.189	4.61	3.97	9000	0.44	-3.7235	-9.3565
67	0.956	.238	.205	1.63	1.40	3000	0.47	-3.6882	-9.3279
68	3.412	.849	.731	6.38	5.49	3000	1.83	-3.1361	-8.7375
69	1.068	.266	.229	1.53	1.32	3000	0.44	-3.6402	-9.3565

Table VII contd.

Run	Starting Pressure (cm.)	moles acid in $\times 10^3$	moles per litre $C_{BA} \times 10^3$	moles CO_2 produced $\times 10^6$	moles CO_2 / litre $\times 10^6$	Reaction Time (Sec.)	Rate CO_2 moles/litre/sec. $\times 10^9$	$\log_{10} C_{BA}$	$\log_{10}$ Rate CO_2
71	0.613	.153	.132	.742	.639	3000	0.21	-3.8794	-9.6716
72	1.623	.404	.348	2.30	1.98	3000	0.66	-3.4584	-9.1805
74	1.468	.365	.314	2.26	1.95	3000	0.65	-3.5031	-9.1871
*75	1.503	.374	.322	2.59	2.23	3000	0.74	-3.4921	-9.1308
77	2.636	.656	.565	3.74	3.22	3000	1.07	-3.2480	-8.9706
*78	2.681	.667	.574	5.48	4.72	3000	1.57	-3.2411	-8.8041
79	2.653	.660	.568	5.67	4.88	3000	1.63	-3.2457	-8.7878
81	0.549	.137	.118	5.78	.497	3000	.166	-3.9281	-9.7799
82	3.751	.934	.804	6.07	5.22	3000	1.74	-3.0947	-8.7595
153	1.761	.4382	.3771	3.16	2.72	3000	.907	-3.4236	-9.0419
155	1.170	.2913	.2507	1.56	1.34	3000	.447	-3.6009	-9.3497
156	3.074	.7650	.6584	6.85	5.90	3000	1.97	-3.1815	-8.7055

TABLE VIII

Initial Rate of Formation of Carbon Monoxide

Temp. 498.5°C., Reactor Volume 1.162 l.

Run	Starting Pressure (cm.)	moles acid in $\times 10^3$	moles per litre $C_{BA} \times 10^3$	moles CO produced $\times 10^6$	CO $\frac{\text{moles}}{\text{litre}} \times 10^6$	Reaction Time (sec.)	Rate CO moles/litre/sec. $\times 10^9$	$\log_{10} C_{BA}$	$\log_{10}$ Rate CO
95	3.395	.8186	.7045	4.78	4.11	1500	2.74	-3.1521	- 8.5622
97	3.186	.7689	.6617	10.82	9.31	2600	3.58	-3.1793	- 8.4461
99	3.158	.7611	.6550	1.12	0.964	600	1.61	-3.1838	- 8.7932
108	0.895	.2160	.1859	0.019	0.016	600	0.027	-3.7307	-10.5686
112	3.183	.7679	.6608	6.95	5.98	2000	2.99	-3.1800	- 8.5243
149	1.602	.3869	.3330	0.768	0.661	1000	0.661	-3.4776	- 9.1798
150	1.630	.3937	.3388	0.472	0.406	1000	0.406	-3.4701	- 9.3915
Temp. 486.0°C.									
158	3.232	.7929	.6824	2.73	2.35	2000	1.18	-3.1659	- 8.9281
159	1.198	.2939	.2529	0.137	0.118	2000	0.059	-3.5971	-10.2291
160	2.443	.5993	.5157	1.33	1.15	2000	0.575	-3.2876	- 9.2403
Temp. 475.1°C.									
153	1.761	.4382	.3771	0.715	0.615	3000	0.205	-3.4236	- 9.6882
155	1.170	.2913	.2507	0.176	0.152	3000	0.051	-3.6009	-10.2950
156	3.074	.7650	.6584	1.39	1.20	3000	0.400	-3.1815	- 9.3979

TABLE IX

Initial Rate of Formation of Hydrogen

Temp. 498.5°C., Reactor Volume 1.162 l.

Run	Starting Pressure (cm.)	moles acid in $\times 10^3$	moles per litre $C_{BA} \times 10^3$	moles H_2 produced $\times 10^6$	moles H_2 / litre $\times 10^6$	Reaction Time (Sec.)	Rate H_2 moles/litre/sec. $\times 10^{11}$	$\log_{10} C_{BA}$	$\log_{10}$ Rate H_2
95	3.395	.8186	.7045	.0361	.0311	1500	2.07	-3.1521	-10.6840
97	3.186	.7689	.6617	.1100	.0947	2600	3.64	-3.1793	-10.4389
99	3.158	.7611	.6550	.0090	.0078	600	1.30	-3.1838	-10.8861
108	0.895	.2160	.1859	.0003	.0003	600	0.045	-3.7307	-12.3468
112	3.183	.7679	.6608	.0538	.0463	2000	2.32	-3.1800	-10.6345
149	1.602	.3869	.3330	.0040	.0034	1000	0.34	-3.4776	-11.4685
150	1.630	.3937	.3388	.0027	.0023	1000	0.23	-3.4701	-11.6421
Temp. 486.0°C.				$\times 10^9$	$\times 10^9$				
158	3.232	.7929	.6824	8.88	7.64	2000	.382	-3.1659	-11.4179
159	1.198	.2939	.2529	1.43	1.23	2000	.0615	-3.5971	-12.2111
160	2.443	.5993	.5157	5.14	4.42	2000	.221	-3.2876	-11.6556
Temp. 475.1°C.				$\times 10^9$	$\times 10^9$				
153	1.761	.4382	.3771	2.36	2.03	3000	.0677	-3.4236	-12.1694
155	1.170	.2913	.2507	1.05	0.904	3000	.0301	-3.6009	-12.5214
156	3.074	.7650	.6584	4.95	4.26	3000	.1420	-3.1815	-11.8477

TABLE X

Initial Rate of formation of $(CO + CO_2)$

Temp. 498.5°C., Reactor Volume 1.162 l.

Run	Starting Pressure (cm.)	moles acid in $\times 10^3$	moles per litre $C_{BA} \times 10^3$	moles $(CO + CO_2)$ produced $\times 10^6$	$(CO + CO_2)$ moles/litre $\times 10^6$	Reac-Time (Sec.)	Rate $(CO + CO_2)$ moles/l./sec. $\times 10^9$	$\log_{10} C_{BA}$	$\log_{10}$ Rate $(CO + CO_2)$
95	3.395	.8186	.7045	18.16	15.63	1500	10.42	-3.1521	-7.9822
99	3.158	.7611	.6550	4.45	3.83	600	6.38	-3.1838	-8.1952
108	0.895	.2160	.1859	1.01.	0.869	600	1.45	-3.7307	-8.8386
112	3.183	.7679	.6608	34.27	29.49	2000	14.75	-3.1800	-7.8312
149	1.602	.3869	.3330	4.32	3.72	1000	3.72	-3.4776	-8.4295
150	1.630	.3937	.3388	3.58	3.08	1000	3.08	-3.4701	-8.5114
Temp. 486.0°C.									
158	3.232	.7929	.6824	9.75	8.39	2000	4.20	-3.1659	-8.3768
159	1.198	.2939	.2529	1.67	1.44	2000	0.72	-3.5971	-9.1427
160	2.443	.5993	.5157	5.75	4.95	2000	2.48	-3.2876	-8.6055
Temp. 475.1°C.									
153	1.761	.4382	.3771	3.88	3.34	3000	1.11	-3.4236	-8.9547
155	1.170	.2913	.2507	1.74	1.50	3000	0.50	-3.6009	-9.3010
156	3.074	.7650	.6584	8.24	7.09	3000	2.36	-3.1815	-8.6271

IV Experiments with Air present

Two initial rate experiments were carried out at 475.1°C. with oxygen in the reaction vessel; in the form of air. The results of these experiments are included in Fig. 14. The experiments were carried out by adding a quantity of air which was one hundred times as much as would leak in (as measured) during an experiment of three thousand seconds duration (approximately 1°/o reaction). Table XII compares these two experiments with two others which are the same with respect to starting concentration and reaction duration but to which no air was added.

TABLE XII

Effect of Added Air

Run Number	74	75	77	78
Number moles benzoic acid in	$.365 \times 10^{-3}$	$.374 \times 10^{-3}$	$.656 \times 10^{-3}$	$.667 \times 10^{-3}$
Number moles acid reacted after 1% reaction	$.00365 \times 10^{-3}$	$.00374 \times 10^{-3}$	$.00656 \times 10^{-3}$	$.00667 \times 10^{-3}$
Pressure of Air added (mm)	-	1.2×10^{-2}	-	2.6×10^{-2}
Number moles O_2 added	-	$.0598 \times 10^{-6}$	-	$.129 \times 10^{-6}$
Number moles O_2 leaked in reaction vessel after 3000 sec.	-	$.000602 \times 10^{-6}$	-	$.00118 \times 10^{-6}$
Total number moles O_2 in reaction vessel	-	$.0604 \times 10^{-6}$	-	$.130 \times 10^{-6}$
Rate of production of CO_2 (moles/litre/sec.)	6.5×10^{-10}	7.4×10^{-10}	10.7×10^{-10}	15.7×10^{-10}

In run number 75 the addition of oxygen equivalent to 1.6 mole percent of the total reacted acid increased the rate of production of carbon dioxide by 13.9°/o over that in run number 74. Similarly, in run number 78 the addition of oxygen equivalent to 1.95 mole percent of the total reacted acid increased the rate of production of carbon dioxide by 46.7°/o over run number 77. Runs 74 and 77 were conditioned initial rate experiments whereas it was impossible to condition the reaction vessel for numbers 75 and 78 since air was being added and admission of air would probably destroy the effect of any conditioning.

V Carbon Monoxide/Carbon Dioxide proportions in products

The data in Table XIII and Fig. 18 show the ratio $\frac{CO}{CO + CO_2}$ as a function of starting concentration of benzoic acid, for initial rate experiments.

VI Experiments with Toluene-d_8 present

These experiments were carried out with various ratios of toluene-d_8 to benzoic acid. Table XIV summarizes the results of the series of toluene-d_8 experiments.

Fig. 19 shows the effect on the C_6H_5D/C_6H_6 ratio of increasing the toluene-d_8/benzoic acid ratio. These are preliminary results.

As can be seen in Table XIV some HD, D_2, and CD_4 were detected in the products of these experiments. In none of the four experiments in which toluene-d_8 was included in the reaction was the total of HD, D_2, and CD_4 equal to more than 2°/o of the carbon dioxide produced in that reaction.

Experiment 140 was carried out in an unconditioned reaction vessel. Numbers 127 and 151 were carried out in a conditioned reaction vessel with no toluene-d_8 present. They are for comparison with numbers 137 and 139, and 147 respectively. Number 128 was carried out in an unconditioned vessel with no toluene-d_8 present.

TABLE XIII

$\frac{CO}{CO + CO_2}$ (as °/o) as a ftn. of moles of Benzoic Acid in Reaction Vessel at start of Reaction.

At 498.5°C. Reaction Time: 600 sec.

Run	moles CO	moles CO_2	moles acid in	$\frac{CO}{CO + CO_2}$ as °/o
95	4.78×10^{-6}	13.38×10^{-6}	$.8186 \times 10^{-3}$	26.32
99	1.12×10^{-6}	3.33×10^{-6}	$.7611 \times 10^{-3}$	25.17
108	$.019 \times 10^{-6}$	$.987 \times 10^{-6}$	$.2160 \times 10^{-3}$	1.89
149	$.768 \times 10^{-6}$	3.55×10^{-6}	$.3869 \times 10^{-3}$	17.79
150	$.472 \times 10^{-6}$	3.11×10^{-6}	$.3937 \times 10^{-3}$	13.18

At 475.1°C. Reaction Time: 3000 sec.

153	$.715 \times 10^{-6}$	3.16×10^{-6}	$.4382 \times 10^{-3}$	18.45
155	$.176 \times 10^{-6}$	1.56×10^{-6}	$.2913 \times 10^{-3}$	10.14
156	1.39×10^{-6}	6.85×10^{-6}	$.7650 \times 10^{-3}$	16.87

At 486.0°C. Reaction Time: 2000 sec.

158	2.73×10^{-6}	8.16×10^{-6}	$.7929 \times 10^{-3}$	25.07
159	$.137 \times 10^{-6}$	1.78×10^{-6}	$.2939 \times 10^{-3}$	7.15
160	1.33×10^{-6}	5.13×10^{-6}	$.5993 \times 10^{-3}$	20.59

TABLE XIV

Comparison of reactions in conditioned and unconditioned vessels, with and without added Toluene-d_8 Temp. 498.5°C.

* - Toluene-d_8 added

\+ - Reaction Vessel not conditioned

Exp. Number	127	151	134	137*
Starting Pressure (cm)	3.243	.950	3.221	3.297
Number moles of Acid in Reactor x 10^3	.7826	.2293	.778	.7958
Number moles of d_8 Toluene in Reactor x 10^3	-	-	-	1.381
Ratio Toluene/Acid	-	-	-	1.74
Number moles CO_2 produced x 10^3	.2494	.07664	.2285	.2543
Number moles CO produced x 10^3	.0768	.01022	.07545	.02688
Number moles H_2 produced x 10^6	.45	.0804	Not Available	.2097
Number moles HD produced x 10^6	-	-	-	.1359
Number moles D_2 produced x 10^6	-	-	-	.1654
Number moles CD_4 produced x 10^6	-	-	-	1.471
$CO/(CO + CO_2) \times 100$ (%)	23.54	11.77	24.82	9.56
Number moles acid unreacted x 10^3	.4152	.1232	Not Available	.4880
Number moles acid reacted x 10^3	.3674	.1061	Not Available	.3078

Table XIV contd.

Exp. Number	127	151	134	137*
% acid unaccounted for	5.26	8.37	Not Available	3.02
Reaction Duration (min)	266.67	266.67	290	266.67
% Reaction	41.68	37.88	38.6	38.67
Ratio $^{*}C_6H_5D/C_6H_6 \times 10^2$	-	-	-	5.79

*ratios from m/e 79/m/e 78 in mass spec.

Table XIV contd.

Exp. Number	139*	147*	140*+	128+
Starting Pressure (cm)	3.310	.951	3.288	3.222
Number moles of Acid in Reactor x 10^3	.7991	.2296	.7951	.778
Number moles of d_8 Toluene in Reactor x 10^3	2.369	7.449	2.602	-
Ratio Toluene/Acid	2.97	32.44	3.27	-
Number moles CO_2 produced x 10^3	.2032	.0963	.4537	.4805
Number moles CO produced x 10^3	.02464	.01519	.04325	.05579
Number moles H_2 produced x 10^6	.1635	.1216	.2854	Not Available
Number moles HD produced x 10^6	.09384	.02467	.1258	-
Number moles D_2 produced x 10^6	.1770	.1322	.2613	-
Number moles CD_4 produced x 10^6	1.164	1.144	2.385	-
$CO/CO + CO_2$ x 100 (%)	10.81	13.62	8.70	10.40 (max.)
Number moles acid unreacted x 10^3	.5320	.1112	.2720	Not Available

Table XIV contd.

Exp. Number	139*	147*	140*+	128+
% acid unaccounted for	4.92	3.01	3.28	Not Available
Reaction Duration (min)	266.67	266.67	266.67	299.36
% Reaction	28.50	48.56	62.50	approx. 68.8
Ratio $^{*}C_6H_5D/C_6H_6$ x 10^2	7.43	13.75	8.10	-

* ratios from m/e 79/m/e 78 in mass spec.

DISCUSSION

I. Products

Assuming that no major products remain undiscovered, and neglecting the polynuclear hydrocarbons, the overall reaction is given by the following combination of reactions;

$$C_6H_5COOH \longrightarrow C_6H_6 + CO_2 \quad (1)$$

$$C_6H_5COOH \longrightarrow C_6H_5OH + CO \quad (2)$$

$$2\ C_6H_5COOH \longrightarrow (C_6H_5)_2 + 2CO_2 + H_2 \quad (3)$$

$$2\ C_6H_5COOH \longrightarrow (C_6H_5)_2 + CO_2 + H_2O + CO \quad (4)$$

(All products except H_2O were identified. The presence of H_2O is postulated).

For reactions carried out in conditioned vessels, at long reaction times, carbon dioxide accounts for greater than 70°/o of COOH and carbon monoxide for the remainder. In unconditioned vessels, with long reaction times, carbon dioxide can account for up to 95°/o of COOH, suggesting that the reaction is simpler in unconditioned vessels.

The contribution of any reaction producing hydrogen is very small since hydrogen accounts for approximately 0.2°/o of the gases; CO, CO_2, and H_2. (See Table VI). Therefore reaction (3) can be ignored as a major part of the total reaction. The contribution of reaction (4) cannot be assessed because no quantitative

analysis for biphenyl has been carried out. A contribution by reaction (4) is consistent with preliminary results of benzene analysis, that is, the molar quantity of benzene was always less than the molar quantity of carbon dioxide. The identification of phenol is tentative and no quantitative analysis for it was undertaken.

Back and Sehon[7, 8] assume that most of the carbon monoxide and carbon dioxide produced in the decompositions of phenylacetic acid and diphenylacitic acid, in the presence of toluene, is formed from the carboxyl radical,

$$.COOH \longrightarrow CO_2 + H.$$

$$.COOH \longrightarrow CO + .OH$$

$$2\ .COOH \longrightarrow 2CO_2 + H_2$$

$$2\ .COOH \longrightarrow CO_2 + CO + H_2O$$

For the phenylacetic acid decomposition[7] they also suggest the possibility of a molecular rearrangement

$$C_6H_5CH_2COOH \longrightarrow C_6H_5CH_3 + CO_2$$

Their results show that reactions forming CO_2 are favoured for phenylacetic acid[7] and also, but to a lesser extent, for diphenylacetic acid[8], the ratio CO/CO_2 being slightly higher in the latter case.

If their CO/CO_2 data are extrapolated down to the temperature range in this work it is found, from the phenylacetic acid results, that the ratio CO/CO_2 goes to zero. This would suggest that no carbon monoxide should be produced in the benzoic acid case. However, if the same

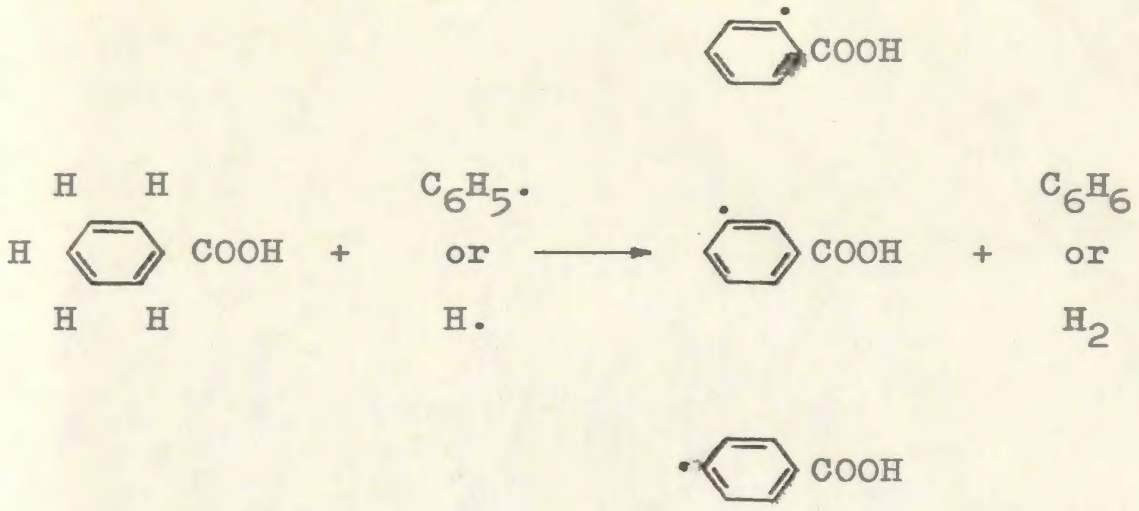
extrapolation is made with the data for diphenylacetic acid it is found that the CO/CO_2 ratio does not become zero at 500°C. but has a value of about 1 : 19. This value is slightly lower than that found for decompositions of benzoic acid in unconditioned vessels and is considerably lower than that found for decompositions in conditioned vessels where the ratio was often as high as 1 : 5. Back and Sehon make no mention of whether or not they conditioned their reaction vessels.

The only marked difference found by Back and Sehon between phenylacetic acid and diphenylacetic acid decompositions was in the extent to which each was affected by the surface of the reaction vessel. The rate of diphenylacetic acid decomposition was found to be strongly dependent on the surface/volume ratio whereas the rate of phenylacetic acid decomposition was only slightly dependent upon the surface/volume ratio. In both cases the ratio CO/CO_2 was increased when the surface/volume ratio was increased. Apparently some of the reactions of the radical .COOH, as well as some of those of phenylacetic acid and diphenylacetic acid, are occuring at the surface.

Blake and Hole[5] detected traces of formic acid in the products in their study of the propionic acid decomposition and a trace of m/e 46 was found in a mass spectral analysis[12] of fraction 3 of the products in an unconditioned experiment in this work (see later). Further

attempts to detect formic acid in the present work[16] were unsuccessful. Back and Sehon[8] also attempted to detect this acid in the products of the decomposition of phenylacetic acid but the large excess of toluene (used as carrier) and the presence of other reaction products made the analysis impossible and positive identification was not made. They did, however, detect a small amount of strong acid which they suspected to be oxalic acid. However, oxalic acid reacts rapidly at approximately 125°c and consequently its detection seems unlikely since Back and Sehon's experiments were carried out at above 500°C. No attempt was made to detect oxalic acid in this present work.

In Table V, some more complicated hydrocarbons are listed, traces of which were detected by mass spectrometry[12] in the reaction products. Since no impurities were detected in the acid itself,[12] one possible explanation for these compounds is that some hydrogen abstraction from the ring occurred, i.e.



This reaction would then be followed by various combinations of these radicals with others present in the reaction vessel or with one another.

II Thermodynamics of the Reaction and Arrhenius Parameters

The heats of formation of some of the species involved in the reaction are listed below in Table XV.

Table XV

$Species_{(g)}$	$\Delta H^{o}_{f25^{o}C}$ (kcal. $mole^{-1}$)	Reference
C_6H_5COOH	-69.9	20
.COOH	-53±3	21
.COOH	-62	7
C_6H_5·	71±2	21
$(C_6H_5)_2$	42.6	21

Table XV (con't)

Species$_{(g)}$	$\Delta H^{o}_{f25^{o}C}$(kcal. mole^{-1})	Reference
C_6H_6	19.8	21
C_6H_5OH	-23.1	21
CO_2	-94.05	21
CO	-26.4	21
H_2O	-57.8	21

Using these values for $\Delta H^{o}_{f25^{o}C}$ and calculating the enthalpy change for the reaction, at 25°C,

$$C_6H_5COOH \longrightarrow C_6H_5\cdot + \cdot COOH \qquad (5)$$

the values obtained are 78.9 kcal. mole^{-1} or 86.9 kcal. mole^{-1}; depending on the value of $\Delta H^{o}_{f25^{o}C}$ used for .COOH. The value obtained, for CO_2 formation, from initial rate experiments in conditioned vessels for the energy of activation is 62.2 kcal. mole^{-1}. Since this value is lower than the bond dissociation energy, D(C_6H_5 - COOH) = 78.9 or 86.9 kcal. mole^{-1}, the main reaction cannot be the homogeneous reaction (5). This statement is substantiated by evidence, discussed in Section III, obtained from preliminary experiments carried out in the presence of toluene -d_8.

Enthalpy changes associated with some relevant reactions are:

Reaction	$\Delta H_{25}{}^{o}{}_{C}$ (kcal. mole^{-1})	Reference
(1) $C_6H_5COOH \rightarrow C_6H_6 + CO_2$	4.4	Table VII
(2) $C_6H_5COOH \rightarrow C_6H_5OH + CO$	20.4	Table VII
(5) $C_6H_5COOH \rightarrow C_6H_5\cdot + \cdot COOH$	78.9 - 86.9	Table VII
$\cdot COOH \rightarrow CO + \cdot OH$	45	7
$\cdot COOH \rightarrow CO_2 + H\cdot$	20	7
$\cdot COOH \rightarrow CO_2 + H\cdot$	12	21

The pre-exponential factor for CO_2 formation is $10^{13.4}$ sec.$^{-1}$ mole$^{-.25}$ l.$^{.25}$ from initial rate experiments in conditioned vessels. This value is within the range associated with homogeneous unimolecular reactions. Although the order is not unity for CO_2 formation (it is 1.2), the enthalpy change and Arrhenius parameters are perfectly consistent with a major contribution from the unimolecular reaction (1).

III Discussion of Reactions with Toluene -d_8 Present.

The results of several preliminary experiments carried out in the presence of toluene -d_8 indicate that approximately 85°/o of the decomposition in conditioned and unconditioned vessels takes place by reactions which do not produce phenyl radicals. The molecular elimination reactions (1) and (2) (surface or gas phase) are suggested.

$$C_6H_5COOH \longrightarrow C_6H_6 + CO_2 \qquad (1)$$

$$C_6H_5COOH \longrightarrow C_6H_5OH + CO \qquad (2)$$

Experiments were carried out with toluene -d_8/benzoic

acid ratios of 1.74, 2.97, 32.4, and 3.27. All but that with a ratio of 3.27 were carried out in conditioned reaction vessels (Table XIV). In order to interpret the results with toluene $-d_8$ it was assumed that phenyl radical reacts mainly via (A) or (B).

$$C_6D_5CD_3 + C_6H_5\cdot \xrightarrow{k_A} C_6H_5D + C_6D_5CD_2\cdot \qquad (A)$$

$$C_6H_5COOH + C_6H_5\cdot \xrightarrow{k_B} C_6H_6 + C_6H_5COO\cdot \qquad (B)$$

giving

$$\frac{d[C_6H_5D]}{dt} = k_A[C_6D_5CD_3][C_6H_5\cdot],$$

$$\frac{d[C_6H_6]}{dt} = k_B[C_6H_5COOH][C_6H_5\cdot],$$

and

$$\frac{d[C_6H_5D]}{d[C_6H_6]} = \frac{k_A[C_6D_5CD_3][C_6H_5\cdot]}{k_B[C_6H_5COOH][C_6H_5\cdot]}$$

For the highest toluene $-d_8$/benzoic acid ratio most phenyl radical reacts via reaction (A) as can be seen in Figure 19. The experiment with the ratio toluene $-d_8$/ benzoic acid of 32.4 showed that no more than 15% of the decomposition occurs by the reaction

$$C_6H_5COOH \longrightarrow C_6H_5\cdot + \cdot COOH \qquad (5)$$

It is difficult to come to any conclusion about the inhibiting effects of toluene $-d_8$ on the reaction (see Table XIV). The rate of production of carbon dioxide, in comparing runs 137 and 127, has not been decreased but the rate of production of carbon monoxide has been decreased by a factor of three, causing a slight inhibition overall.

Comparing run 139 with runs 137 and 127, run 139 having a higher toluene -d_8/benzoic acid ratio than run 137, it can be seen that the reaction producing carbon dioxide has now been inhibited while the rate of carbon monoxide formation was unchanged from that in run 137.

The results do not establish a relationship between toluene -d_8 pressure and rate of reaction, and toluene -d_8 pressure and the carbon monoxide/carbon dioxide ratio. Initial rate studies to determine rate and order at various toluene -d_8 pressures are required since the rate differentials would be more pronounced in the earlier stages of the decomposition. Also knowledge of the ratio C_6H_5D/C_6H_6 in this initial period would be useful for comparison with those results obtained after long reaction times.

One experiment was carried out in the presence of toluene -d_8 in an unconditioned reaction vessel. The rate of reaction, $d[CO_2 + CO]/dt$, in this experiment, run 140, is higher than a corresponding reaction in a conditioned vessel, run 137. This is not unexpected since reactions in unconditioned vessels were always faster than those in conditioned vessels. The ratio $CO/(CO + CO_2)$ is also of approximately the same value as that for reactions in unconditioned vessels without toluene -d_8; c.f. run 128.

The ratio of C_6H_5D/C_6H_6 in an unconditioned vessel (run 140) falls on the curve (Fig. 19) composed

of data obtained from reactions in conditioned vessels. This indicates that the reaction which takes place in unconditioned vessels and does not occur, or is inhibited, in conditioned vessels and which produces carbon dioxide thereby lowering the ratio $CO/(CO + CO_2)$, does not produce phenyl radicals. If this reaction produced phenyl radicals an increase in the C_6H_5D/C_6H_6 ratio would be expected in unconditioned vessels. The results indicate that the heterogeneous reaction

$$C_6H_5COOH \longrightarrow C_6H_6 + CO_2 \qquad (1)$$

is important.

Other reactions of toluene also occur and the small quantities of CD_4, HD, and D_2 in the products of experiments carried out in the presence of toluene $-d_8$ can be explained when these are considered.

$$C_6D_5CD_3 \longrightarrow C_6D_5\cdot + \cdot CD_3$$

$$\cdot CD_3 + C_6D_5CD_3 \longrightarrow C_6D_5CD_2\cdot + CD_4$$

It has been stated by Szwarc[15] that the first step in the toluene pyrolysis is

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2\cdot + H\cdot$$

Extrapolating to the case of the deuterated species

$$C_6D_5CD_3 \longrightarrow C_6D_5CD_2\cdot + D\cdot$$

$$D\cdot + C_6D_5CD_3 \longrightarrow D_2 + C_6D_5CD_2\cdot$$

$$C_6D_5CD_3 + H\cdot \longrightarrow C_6D_5CD_2\cdot + HD$$

The small quantities of CD_4 indicate that little $C_6D_5\cdot$ was formed (see Table XIV). As can be seen in Table XIV,

in only one case, run 147, did the quantity of $H_2 + D_2 + HD + CD_4$ exceed .7°/o of the total ($CO_2 + CO + H_2 + D_2 + HD + CD_4$) and it was then only 1.2°/o. Consequently reactions producing any of these hydrogenated or deuterated products may be neglected and the extent of pyrolysis of toluene -d_8 is negligible.

The fate of the benzyl radical, as suggested by Back and Sehon,[7] and Szwarc,[15] could be dimerization.

$$2\ C_6D_5CD_2\cdot \longrightarrow (C_6D_5CD_2)_2$$

or $$C_6D_5CD_2\cdot + \cdot COOH \longrightarrow CO_2 + C_6D_5CD_2H$$

No analyses for $(C_6D_5CD_2)_2$ or $C_6D_5CD_2H$ were undertaken.

IV Discussion of Radical Reactions

The presence of C_6H_5D and biphenyl shows that the phenyl radical is produced, presumably <u>via</u> the homogeneous or heterogeneous reaction (5). Reactions (6) - (12) are the major reactions expected to follow (5).

$$C_6H_5COOH \xrightarrow{k_5} C_6H_5\cdot + \cdot COOH \qquad (5)$$

$$C_6H_5\cdot + C_6H_5COOH \xrightarrow{k_6} C_6H_6 + C_6H_5CO_2\cdot \qquad (6)$$

$$C_6H_5CO_2\cdot \xrightarrow{k_7} CO_2 + C_6H_5\cdot \qquad (7)$$

$$C_6H_5\cdot + C_6H_5\cdot \xrightarrow{k_8} (C_6H_5)_2 \qquad (8)$$

$$\cdot COOH + M \xrightarrow{k_9} CO_2 + H\cdot + M \qquad (9)$$

$$\cdot COOH + M \xrightarrow{k_{10}} CO + \cdot OH + M \qquad (10)$$

$$H. + C_6H_5COOH \xrightarrow{k_{11}} H_2 + C_6H_5CO_2. \qquad (11)$$

$$.OH + C_6H_5COOH \xrightarrow{k_{12}} H_2O + C_6H_5CO_2. \qquad (12)$$

This mechanism gives the following rate expression;

$$\frac{d[CO_2]}{dt} = k_5[BA] + \frac{k_6}{k_7}\left(\frac{k_5}{k_8}\right)^{1/2}[BA]^{3/2} + \frac{k_5k_9}{k_9 + k_{10}}[BA],$$

where BA = C_6H_5COOH.

For long chains the order would be 1.5 but for short chains the order would be between 1.0 and 1.5. This mechanism would provide an explanation of the 1.25 order for carbon dioxide production (Fig. 14) if it were the main mechanism. However the results of experiments in toluene -d_8 indicate that the reaction is mainly the molecular reaction (1). The order might arise from a mixture of molecular and long chain radical reactions. Inhibition by toluene -d_8 would be expected if the reaction is partly a chain reaction. Careful initial rate experiments, with toluene -d_8 present, should be carried out in an attempt to detect inhibition and change in order.

An imbalance for carboxyl group was found (Table VI) which was least pronounced early and later in the decomposition. Also, pressure vs. time curves (Fig. 13) show a slight upward curvature, as does a ($CO + CO_2$) vs. time curve, indicating catalysis by some

intermediate or a slow radical buildup but there is no evidence for a chain reaction. Formic acid, mentioned earlier, should be considered when trying to account for the missing carboxyl. This compound could be formed by either of the two following reactions:

$$.COOH + C_6H_5COOH \longrightarrow HCOOH + C_6H_5CO_2. \qquad (C)$$

$$.COOH + .COOH \longrightarrow HCOOH + CO_2 \qquad (D)$$

In this temperature range formic acid is known to decompose to carbon dioxide, hydrogen, carbon monoxide, and water; the stoichiometry depending upon the surface, temperature, and pressure.[1] If reaction (E),

$$HCOOH \longrightarrow CO_2 + H_2 \qquad (E)$$

is an elementary reaction then it is not significant since very little hydrogen was detected. However if reactions (E_1) or (E_2) occur instead,

$$HCOOH \longrightarrow H. + .COOH \qquad (E_1)$$

$$HCOOH \longrightarrow HCOO. + H \qquad (E_2)$$

the small amount of hydrogen does not necessarily mean that reactions (E_1) or (E_2) are unimportant since reactions such as (F) could take place

$$H. + C_6H_5. \longrightarrow C_6H_6 \qquad (F)$$

The lack of hydrogen in the products also suggests that if H. is produced by reaction (9) or by reactions (E_1), (E_2), then H. does not react appreciably by abstraction but more likely by recombination with another radical as

in reaction (F).

For carbon monoxide and hydrogen production the chain mechanism gives

$$\frac{d[CO]}{dt} = \frac{k_5 k_{10}}{k_9 + k_{10}} [C_6H_5COOH]$$

$$\frac{d[H_2]}{dt} = \frac{k_5 k_9}{k_9 + k_{10}} [C_6H_5COOH]$$

indicating that the reactions producing carbon monoxide and hydrogen are first order. This contradicts the preliminary observation, for initial rate experiments, that the order for carbon monoxide production is approximately two (Fig. 15). Initial rate experiments also indicate that the order for hydrogen production is greater than one (Fig. 16). Apparently the chain mechanism is not important, or, there is another source of carbon monoxide and another source of hydrogen. Of course, reaction (10) is not significant at this temperature if the extrapolated value of the CO/CO_2 ratio is used from Back and Sehon's[7,8] work. (See I Products). Also, on the basis of the order, reaction (2)

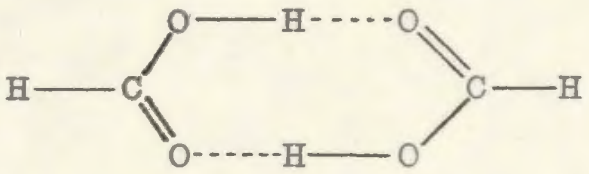
$$C_6H_5COOH \longrightarrow C_6H_5OH + CO,$$

does not contribute significantly to the formation of carbon monoxide.

V Comments on CO and H_2 Production

Preliminary calculation of the Arrhenius parameters for carbon monoxide production, on the basis that the

reaction is second order, gives an activation energy of 61.4 kcal. $mole^{-1}$ and $A = 10^{15.4}$ l. $mole^{-1}sec.^{-1}$ The pre-exponential factor is much greater than that found by Blake and Hinchelwood[1] for the second order production of carbon monoxide from formic acid in carbon coated vessels ($A = 10^{7.46}$ l. $mole^{-1}sec.^{-1}$). They suggested that the order and pre-exponential factor were consistent with the unimolecular decomposition of formic acid dimers, or with the bimolecular decomposition of monomers. They state that the accepted molecular structure of formic acid dimer,



is especially suited sterically to a decomposition to carbon monoxide and water. How this would occur is not immediately obvious.

One suggestion for the production of carbon monoxide and hydrogen from benzoic acid is that carboxyl radicals react at the surface:

$$.COOH_{adsorbed} + .COOH_{adsorbed} \longrightarrow CO + CO_2 + H_2O \quad (G)$$

or $$.COOH_{adsorbed} + .COOH_{adsorbed} \longrightarrow 2CO_2 + H_2 \; ; \quad (H)$$

where the concentration of $.COOH_{adsorbed}$ is proportional to the pressure of benzoic acid. Here the order for carbon monoxide and hydrogen production would be two. A contribution to the total production of carbon dioxide by the

formation of some of the carbon dioxide via a second order mechanism, such as that above, would be consistent with the fact that the observed order for carbon dioxide formation is greater than unity.

VI Effect of Conditioning Reaction Vessel.

The need for conditioning the reaction vessel, the resulting decrease in the rate of reaction, and the change in the $CO/(CO + CO_2)$ ratio upon conditioning suggest that some of the reaction takes place on the surface of the reaction vessel. The rates of pyrolysis of other acids also are sensitive to the surface conditions. Bamford and Dewar[3] found that, in the acetic acid decomposition, "the results were very dependent on the surface of the reaction vessel, but became reproducible after a number of runs had been done without cleaning the tube". In their investigation of the pyrolysis of propionic acid, Blake and Hole[5] state that "since a rapid surface reaction takes place on silica, the vessel walls were coated with carbon by the repeated pyrolysis of isobutane, until the rate of the decomposition fell to a reproducible minimum value". Blake and Pritchard[4], studying the thermal decomposition of trifluosoacetic acid, found it necessary to repeatedly pyrolyse trifluoroacetic acid at 380°. The two silica vessels used (packed and unpacked) gave reproducible rates after this treatment but the mild

steel vessel used gave results which continued to decrease slowly. Blake and Hinshelwood[1] also found that the decomposition of formic acid was dependent on the condition of the surface of the silica reaction vessel. They laid down a film of carbon on the vessel's walls to suppress reactions occuring at the surface. The significance of these observations with regard to conditioning of the surface of the reaction vessels is not stated for any of these studies and it is difficult to understand exactly what happens other than that the carbon film in some way "deactivates" the surface of the vessel. In this present study the surface of the reaction vessel, when the vessel was dismantled after the experimental work, was found to be clean, showing no signs of a carbon film. (This finding substantiates the fact that no hydrocarbons which could be due to fragmentation of the ring were found in the products.

In decompositions of benzoic acid in which no toluene -d_8 (the effect of conditioning the reaction vessel on decompositions in the presence of toluene -d_8 has been described previously) had been added to the reaction vessel, conditioning had the effect of lowering the overall rate of decomposition $d(CO + CO_2)/dt$. In Table XIV, comparing runs 127, 134, and 128, it can be seen that, on conditioning, the quantity of carbon dioxide produced decreased by 50°/o and that carbon monoxide increased by approximately 40 - 50°/o. Since most of the total ($CO + CO_2$) is composed of carbon dioxide, the overall rate decreased.

These results suggest that a reaction which produces carbon dioxide in decompositions in unconditioned vessels is absent or, at least, inhibited in decompositions carried out in conditioned vessels. Such a reaction could be the surface reaction

$$C_6H_5COOH_{adsorbed} \longrightarrow CO_2 + C_6H_6 \qquad (J)$$

Also it would appear that reaction (G)

$$2\ .COOH_{adsorbed} \longrightarrow CO + CO_2 + H_2O \qquad (G)$$

or some other reaction producing carbon monoxide is accelerated by conditioning. The contribution of reaction (H)

$$2\ .COOH_{adsorbed} \longrightarrow 2CO_2 + H_2 \qquad (H)$$

cannot be significant for carbon dioxide production under any conditions because of the lack of hydrogen produced. Unconditioned initial rate experiments gave very erratic results, and probably no useful kinetic experiments are obtainable.

One possible explanation of the conditioning phenomenon is that the reaction vessel surface might be "deactivated" by benzoic acid molecules for a decomposition which immediately followed this deactivation (i.e. conditioning). Reactions with various surface/volume ratios are needed to further investigate the extent of any surface reaction which occurs.

As described in the "Results" section, two initial rate experiments were carried out in the presence

of small amounts of added air (Table XII) to determine whether irreproducability was due to a small and variable amount of air leaking into the vessel. The air was added to the reaction vessel prior to the introduction of the benzoic acid. Fig. 14 shows that the air had only a slight accelerating effect on the rate of the decomposition. If the reaction vessel was closed off after the last experiment for the day was completed and not pumped overnight it was found that the rate of reaction in the first experiment on the following day was in the reproducible region. When the reaction vessel was pumped overnight it was found that conditioning was necessary to obtain reproducible rates of reaction.

There are several ways of treating the reaction vessel overnight in order to produce different effects on the experiment which followed:

1. Reaction vessel standing closed all night in which case the air pressure might be fairly high, at least higher than in a diffusion pumped vessel.
2. Reaction vessel pumped overnight with fore-pump only. This would have a constant pressure of 10^{-3} to 10^{-4} mm. of air in the vessel.
3. Reaction vessel pumped overnight with fore-pump and diffusion pump. The pressure

would be maintained at about 10^{-6}mm.

No obvious differences between reactions carried out after 2 or 3 were observed. The fact that following 2 and 3 conditioning was required to obtain reproducible rates of reaction, whereas after 1 it was not, indicates that it is the pumping which "deconditions" the reaction vessel rather than a small amount of air. However, venting the reaction vessel to the atmosphere deconditions the vessel to such an extent that several experiments are necessary to condition it again (Fig. 20). It does not seem possible to relate these observations to Semenov's comments[22] on the effects of oxygen on the rates of decomposition of organic compounds.

VII Summary

The results of this study can be interpreted as follows:

1. The reaction is mainly the homogeneous or heterogeneous molecular reaction
   $C_6H_5COOH \longrightarrow C_6H_6 + CO_2$
2. Some phenyl radical is formed.
3. There is, as yet, no evidence for a chain reaction, however this aspect of the decomposition deserves further detailed study.
4. The order for carbon monoxide and hydrogen formation is apparently greater than unity.

5. The Arrhenius parameters for carbon dioxide formation are consistent with those of a homogeneous unimolecular reaction.
6. The order of 1.25 for carbon dioxide and the high order for hydrogen and carbon monoxide can be explained by assuming heterogeneous reactions of .COOH.
7. After repeated experiments, apparently the rate of the heterogeneous reaction

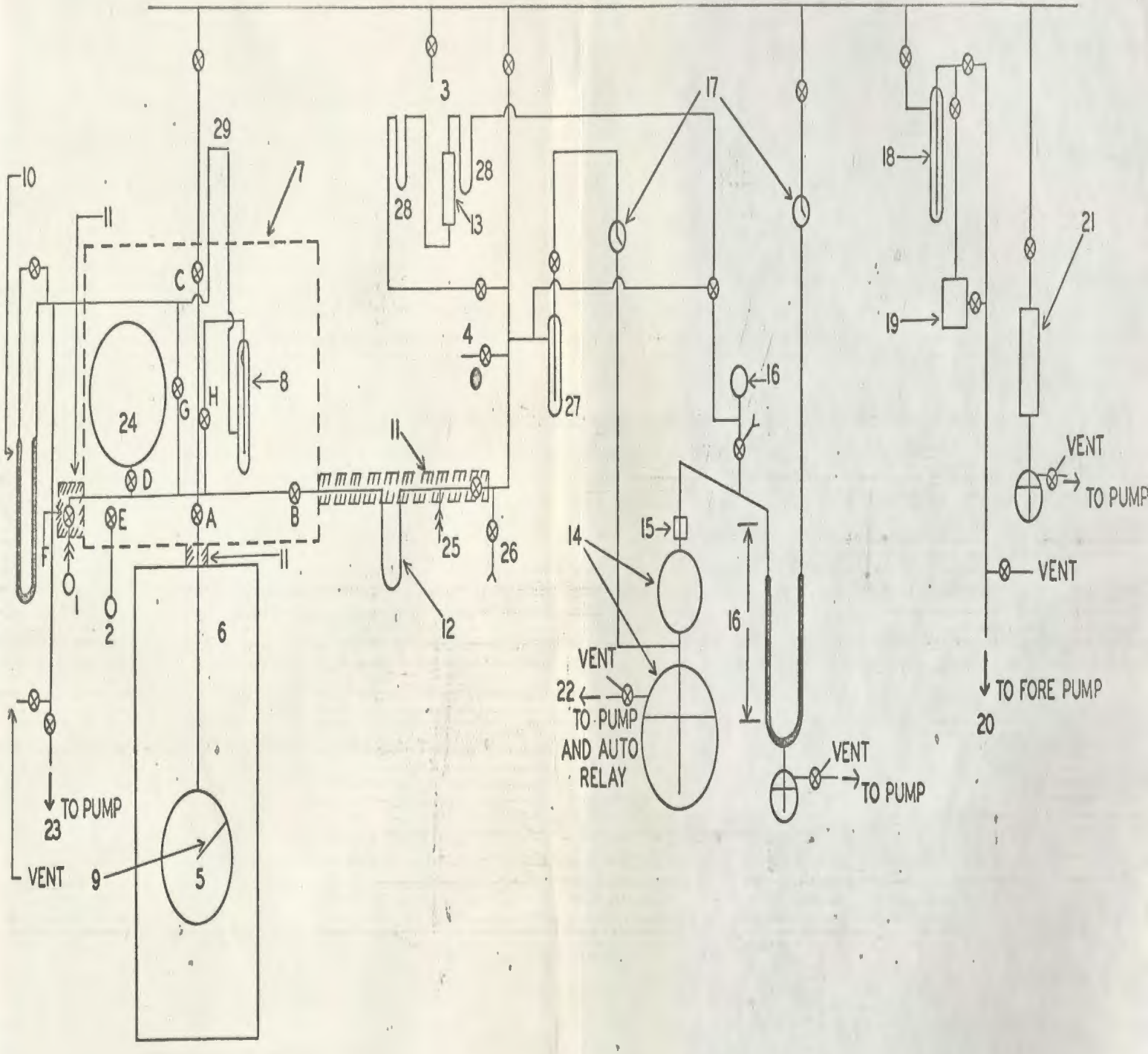
   $C_6H_5COOH \longrightarrow C_6H_6 + CO_2$

   is decreased.

It is obvious that more work is necessary to fully understand the decomposition of benzoic acid. For the reasons mentioned earlier, the most pressing investigations are a study of surface effects and a study of the carbon monoxide producing reaction. The work with toluene $-d_8$ is far from complete and requires extending to the study of initial rates of reaction. More information on the free radical part of the decomposition should come from studies with inhibitors and changes in the surface; both by increasing the surface/volume ratio and investigating the reaction in carbon coated vessels.

Figure 1

Apparatus Diagram



APPARATUS DIAGRAM

Key to Apparatus Diagram

Figure 1

1. Toluene-d_8 Storage bulb (removeable)
2. Benzoic Acid Storage bulb
3. Thermocouple Gauge Takeoff Point (TC-1)
4. Thermocouple Gauge Takeoff Point (TC-2)
5. Reaction Vessel (See figure 2)
6. Reaction Furnace (See figure 6)
7. Hot Box (contents heated)
8. Spoon Gauge (See figure 3)
9. Thermocouple Well
10. Manometer
11. Heated Winding
12. Main U-trap for Product Separation
13. Copper Oxide Furnace
14. Toepler Pump (See figure 7)
15. Float Valve
16. Measured Volume
17. Mercury Splash Trap
18. Main Pump-protecting Trap
19. Oil Diffusion Pump
20. Fore Pump
21. McLeod Gauge
22. Pump and Automatic Relay
23. Pump for Spoon Gauge 8 and Manometer 10
24. Five Litre Bulb

Key to Apparatus Diagram Figure 1.

25. Removable Finger for Solids

26. Takeoff Point for Finger for Gaseous Products

27. Secondary Product Separation Trap

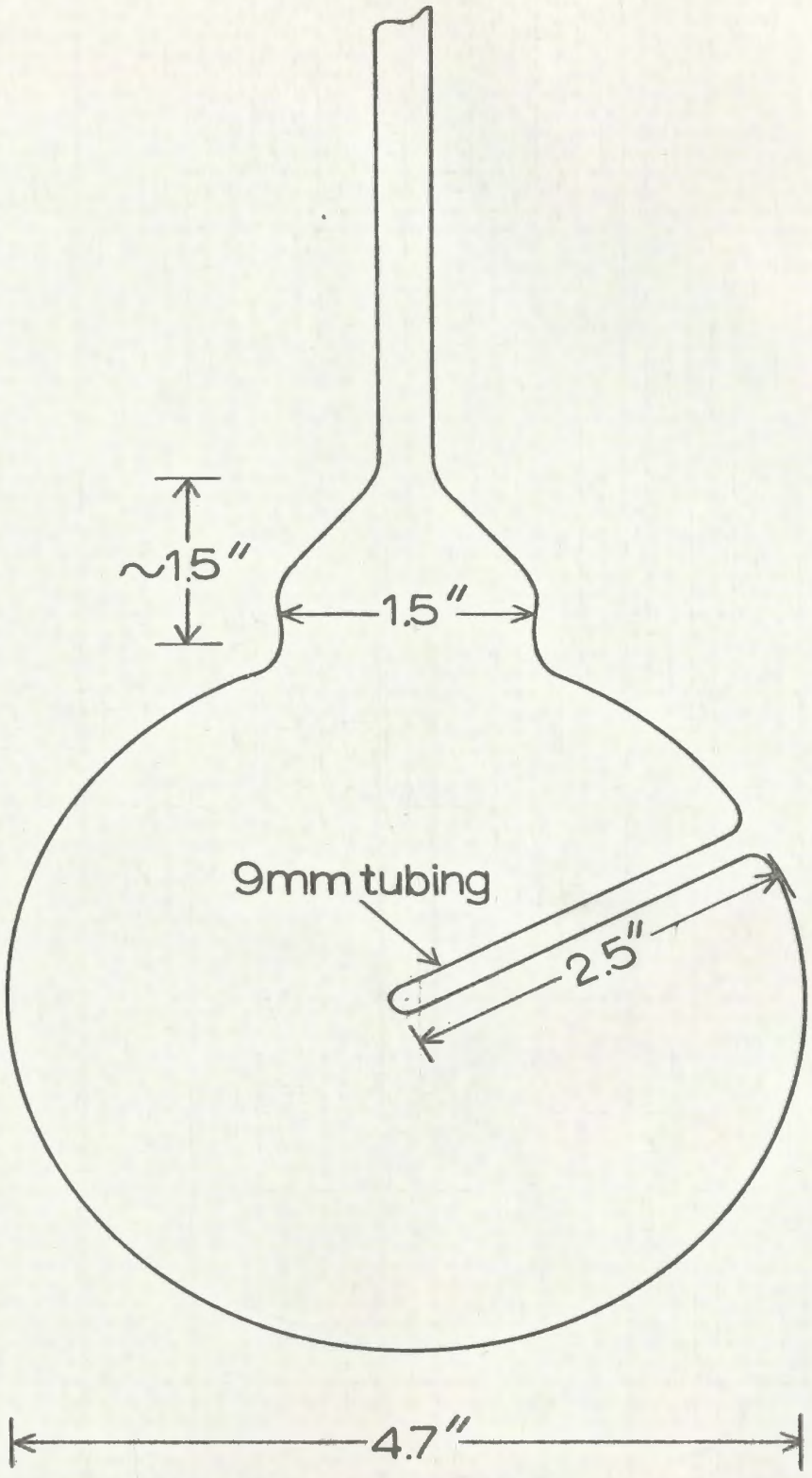
28. Copper Oxide protection Trap

29. Inverted U-Trap for Silicon Oil

a.-h. Stopcocks in Vicinity of Hotbox.

Figure 2

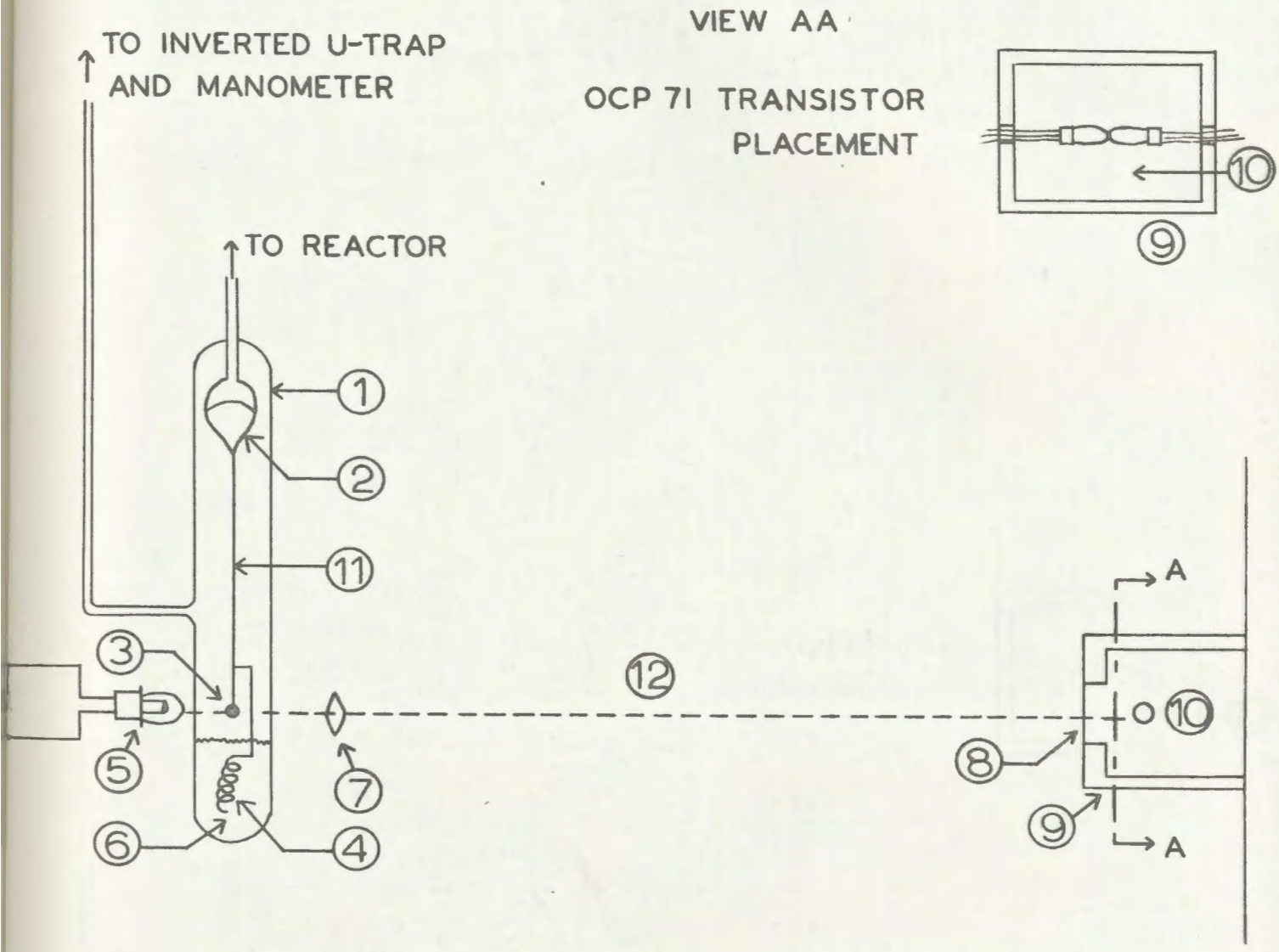
The Reaction Vessel



REACTION VESSEL

Figure 3

Spoon Gauge and Phototransistors



SPOON GAUGE AND PHOTOTRANSISTORS

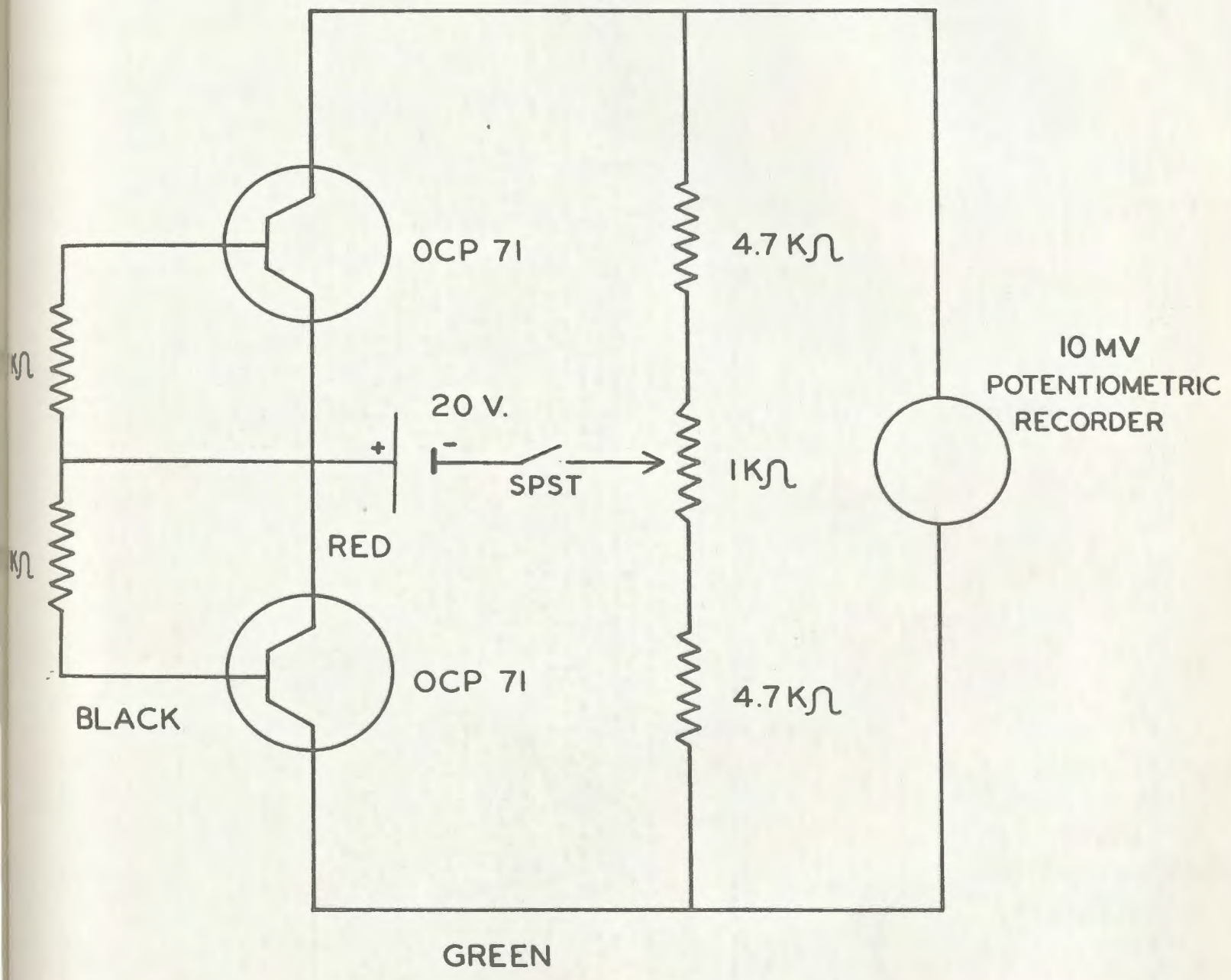
Key to Spoon Gauge and Phototransistors

Figure 3

1. Spoon Gauge outer envelope
2. Spoon
3. Glass Ball
4. Glass Spiral for damping
5. 12v. automotive headlight bulb
6. Dow Corning 200 silicon damping fluid
7. Focusing Lens
8. Window
9. Insulated and Cooled Box
10. OCP 71 Phototransistors
11. Pointer Arm
12. Light Path (approximately 3 ft.)

Figure 4

Phototransistor Circuit



DOUBLE PHOTOTRANSISTOR CIRCUIT USED IN PRESSURE MEASUREMENT

Figure 5

Stopcock Remote Control
used for Air Furnace Stopcocks

Figure 6

Furnace and Reaction Vessel

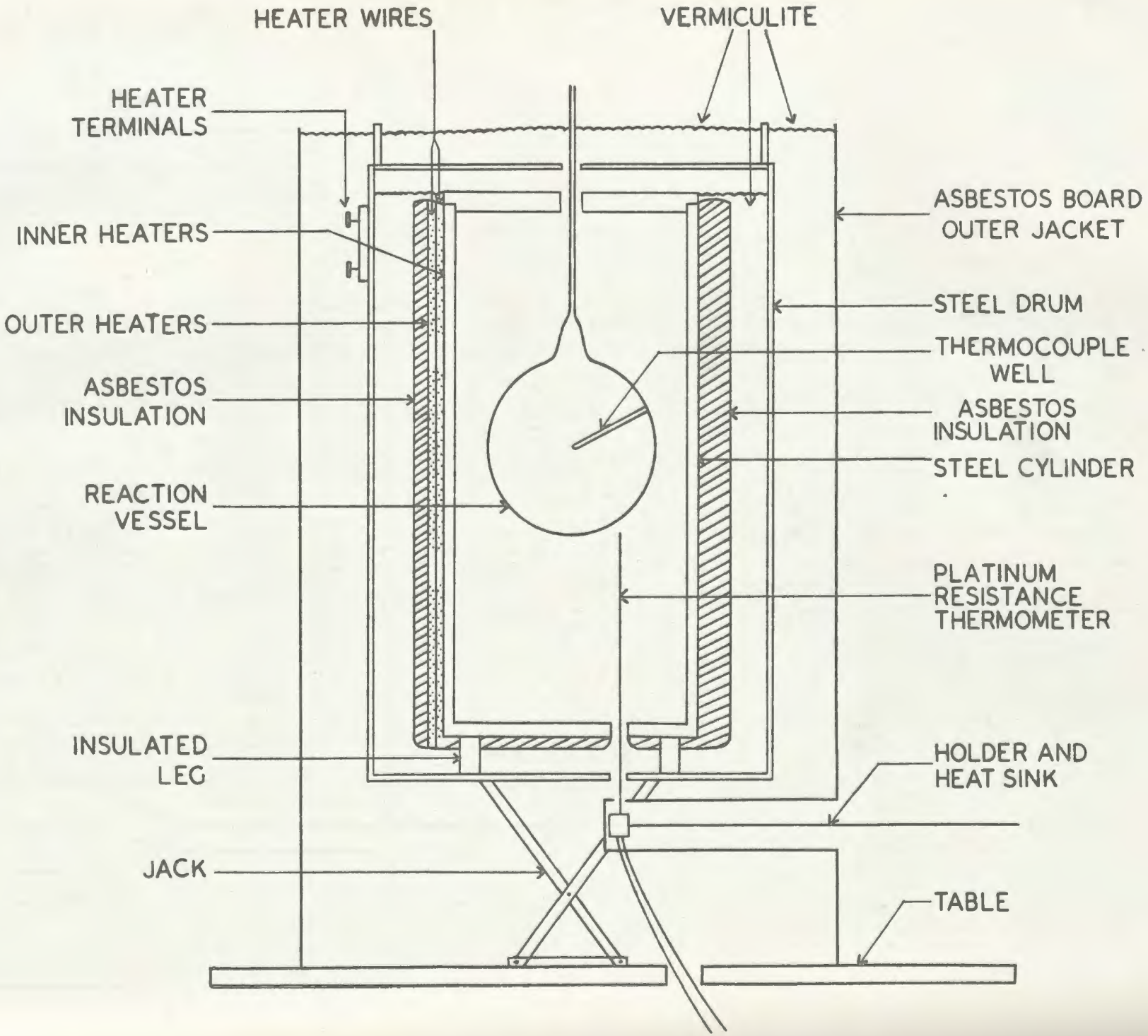

HEATER WIRES
VERMICULITE
HEATER TERMINALS
INNER HEATERS
OUTER HEATERS
ASBESTOS INSULATION
REACTION VESSEL
INSULATED LEG
JACK
ASBESTOS BOARD OUTER JACKET
STEEL DRUM
THERMOCOUPLE WELL
ASBESTOS INSULATION
STEEL CYLINDER
PLATINUM RESISTANCE THERMOMETER
HOLDER AND HEAT SINK
TABLE

Figure 7

Measured Volume and Toepler Pump

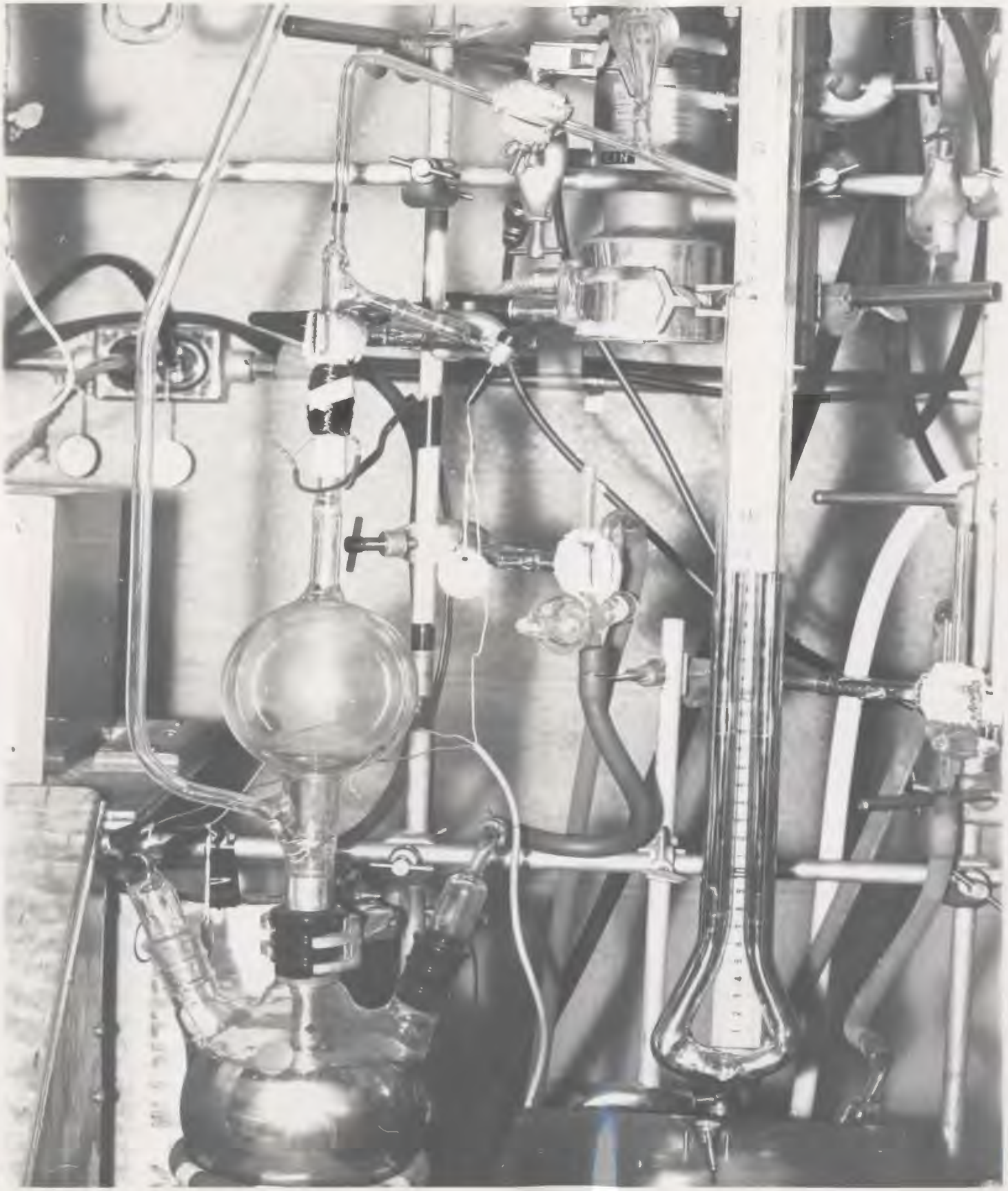


Figure 8

Infrared Spectrum

of

Pure Benzene

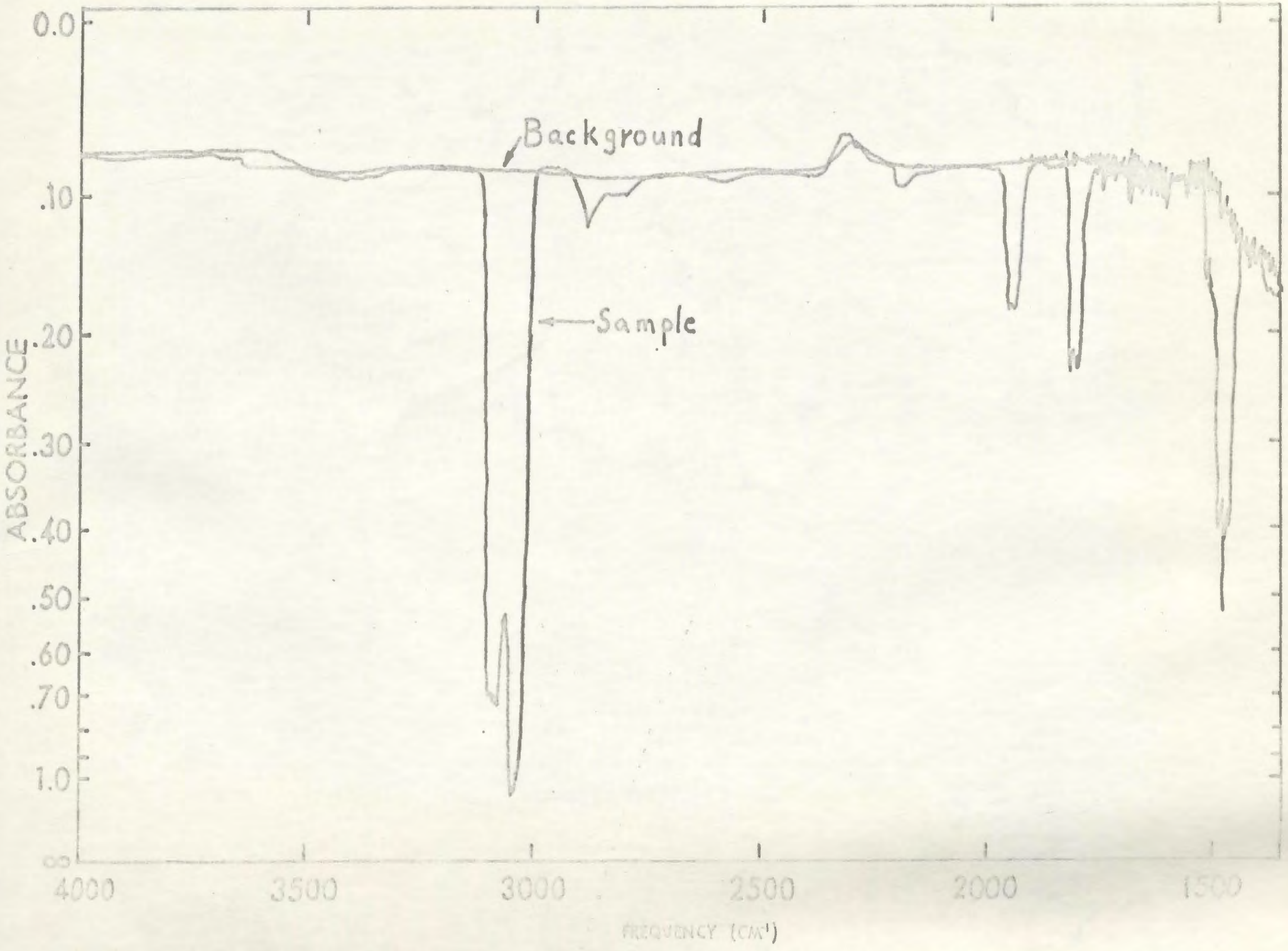

0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
ABSORBANCE
Background
Sample
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

Figure 8a

Infrared Spectrum of 0°C. Fraction of Reaction Products.

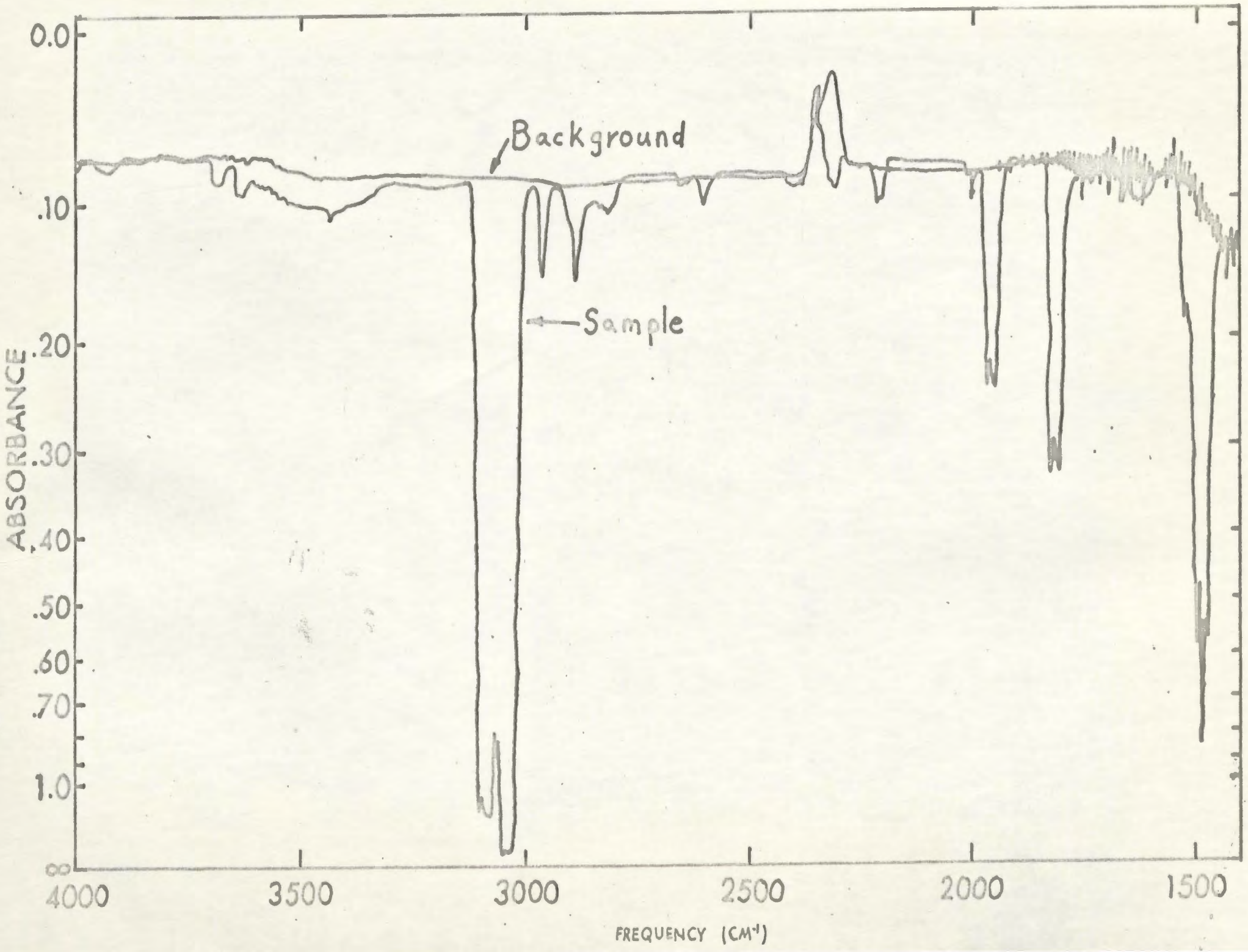

0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
ABSORBANCE
Background
Sample
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

Figure 9

Benzene Infrared Calibration Curve

(Absorbance vs. No. moles C_6H_6.)

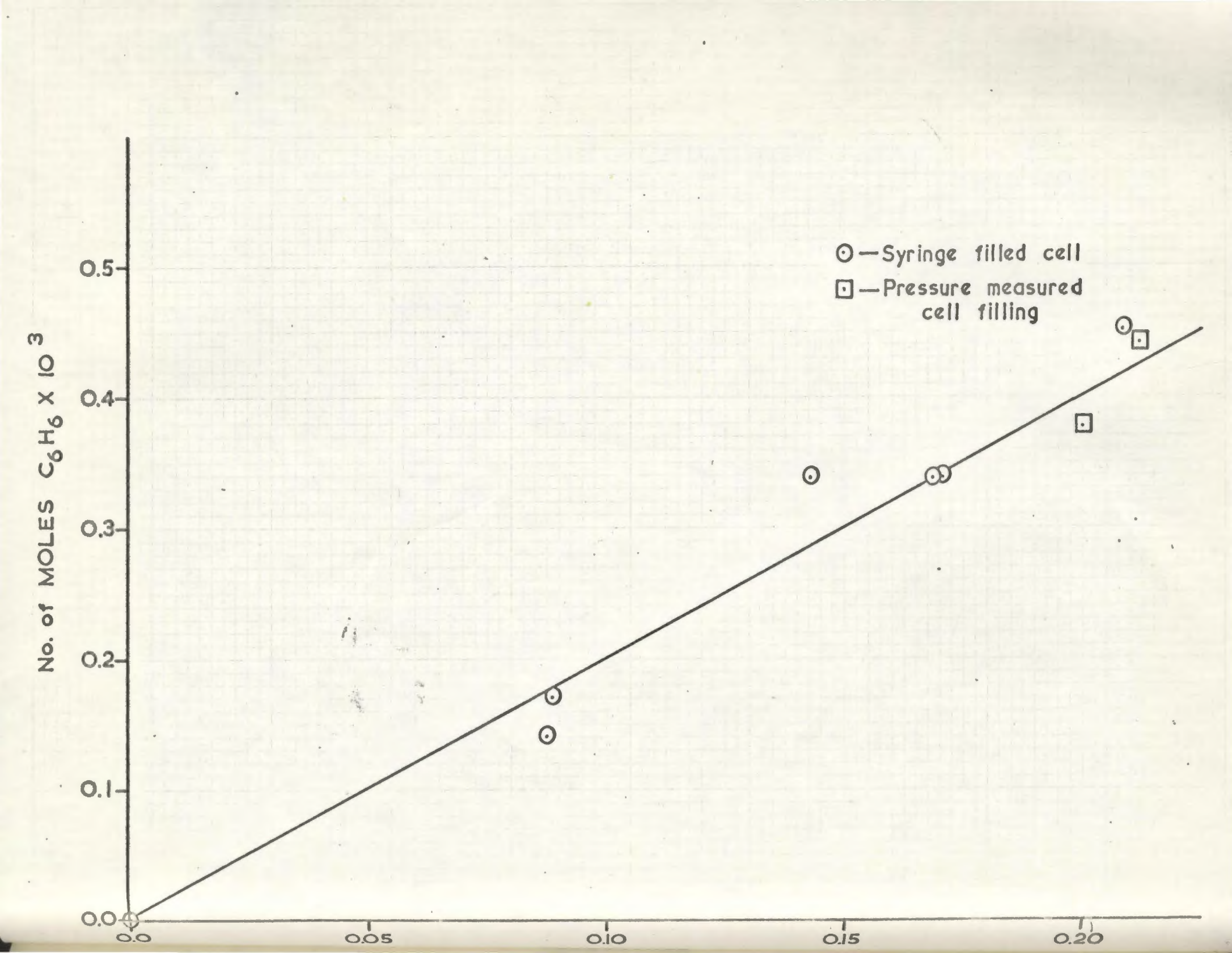

⊙—Syringe filled cell
⊡—Pressure measured cell filling
No. of MOLES C_6H_6 X 10^3
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.05
0.10
0.15
0.20

Figure 10

General View of Apparatus
(showing right hand side of Fig. 1)

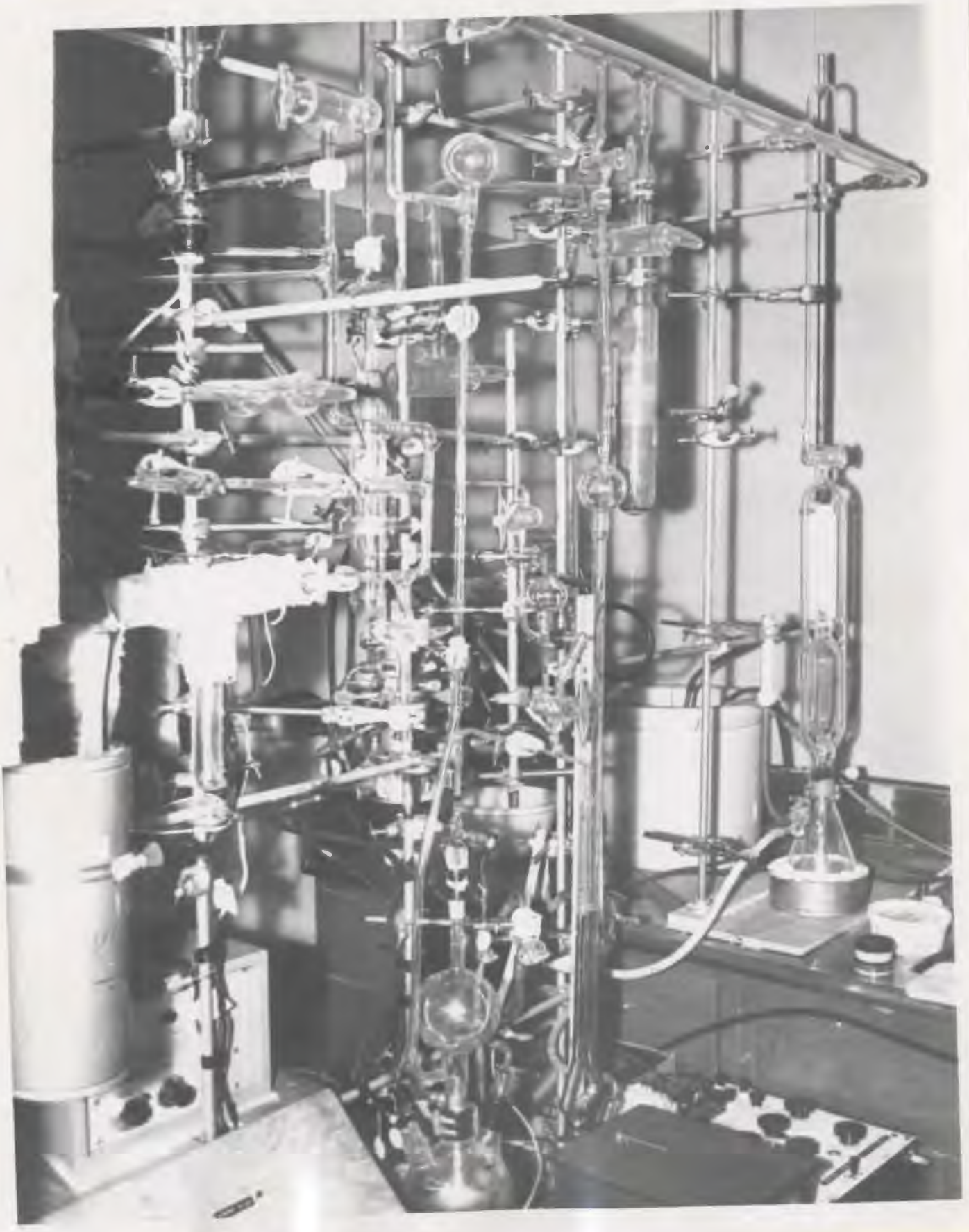


Figure 11

General View of Apparatus
(showing left hand side of Fig. 1.)

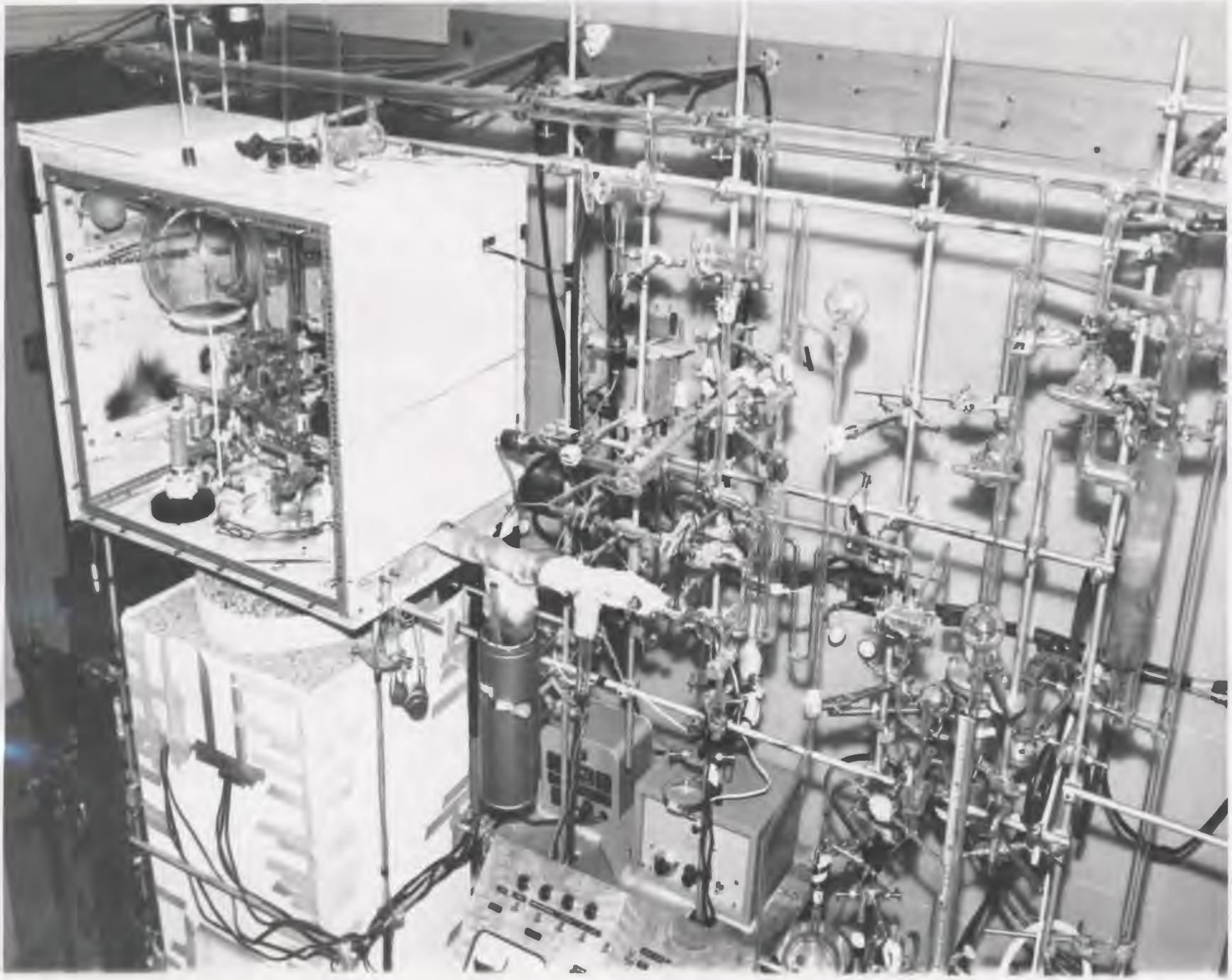


Figure 12

Air Furnace and upper portion
of Reactor Furnace

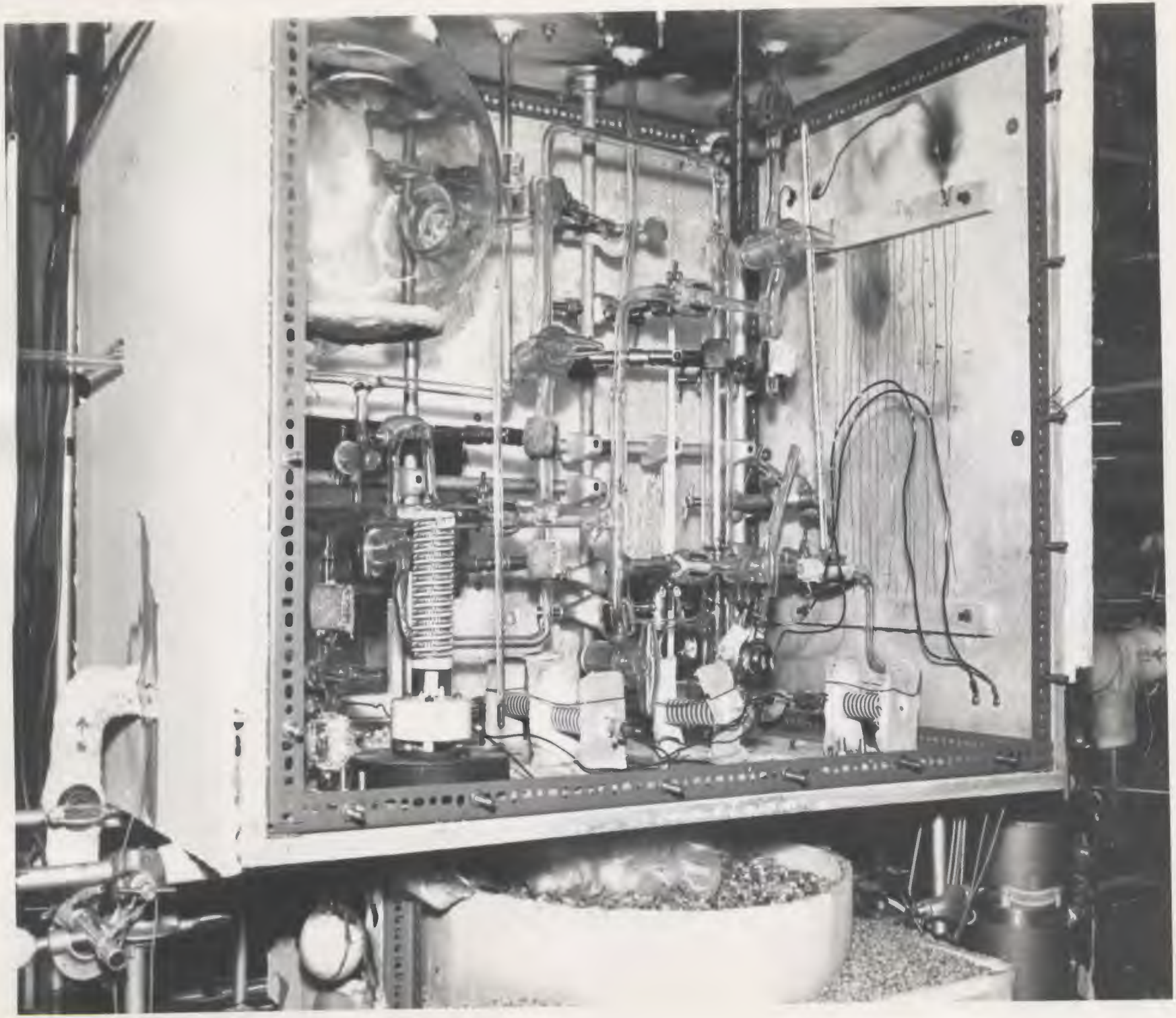


Figure 13

Pressure-Time Curves for decompositions
in Conditioned and Unconditioned reaction vessels
at 498.5°C

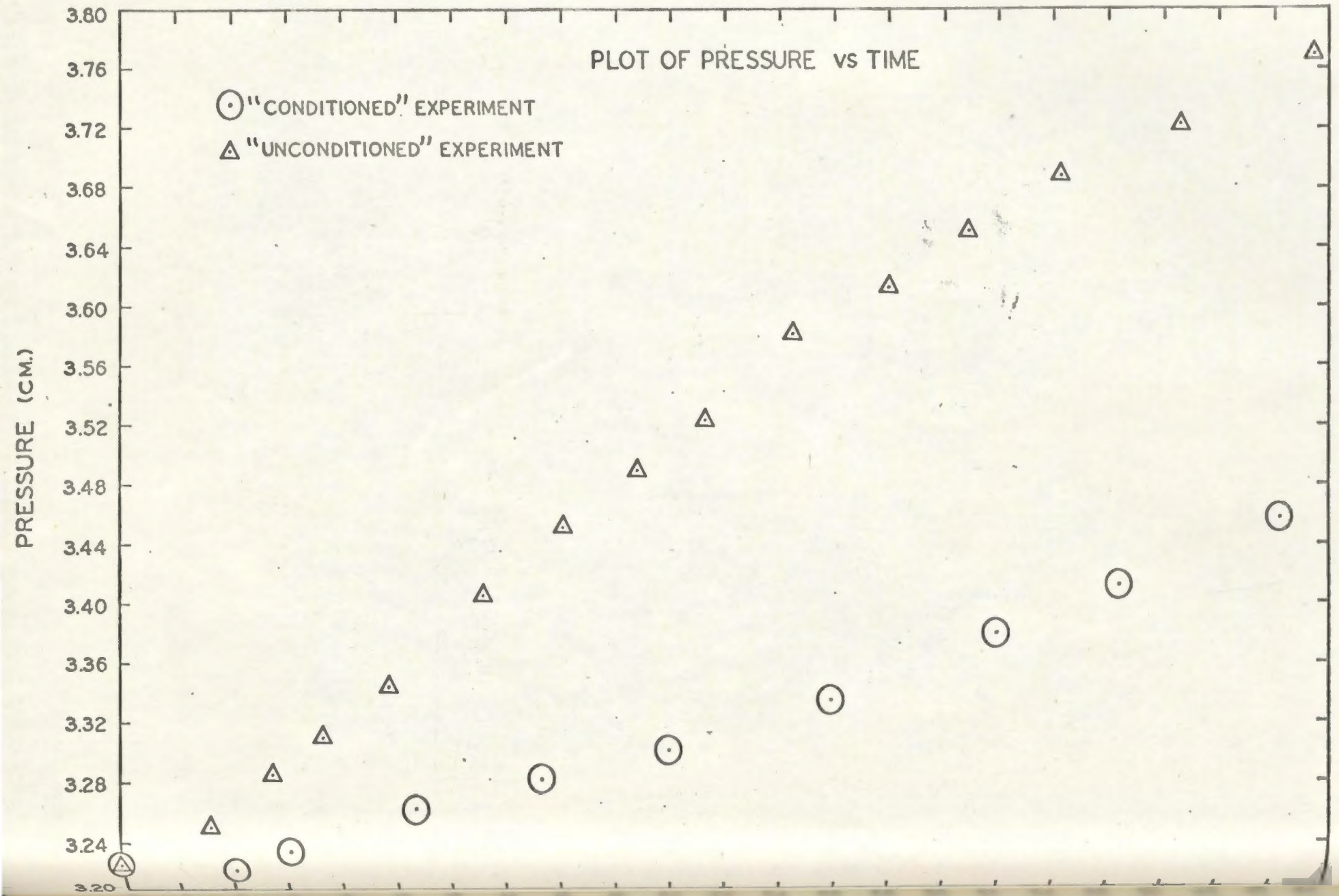

PLOT OF PRESSURE vs TIME
"CONDITIONED" EXPERIMENT
"UNCONDITIONED" EXPERIMENT
PRESSURE (CM.)
3.80
3.76
3.72
3.68
3.64
3.60
3.56
3.52
3.48
3.44
3.40
3.36
3.32
3.28
3.24
3.20

Figure 14

Initial Rates of Formation of Carbon Dioxide

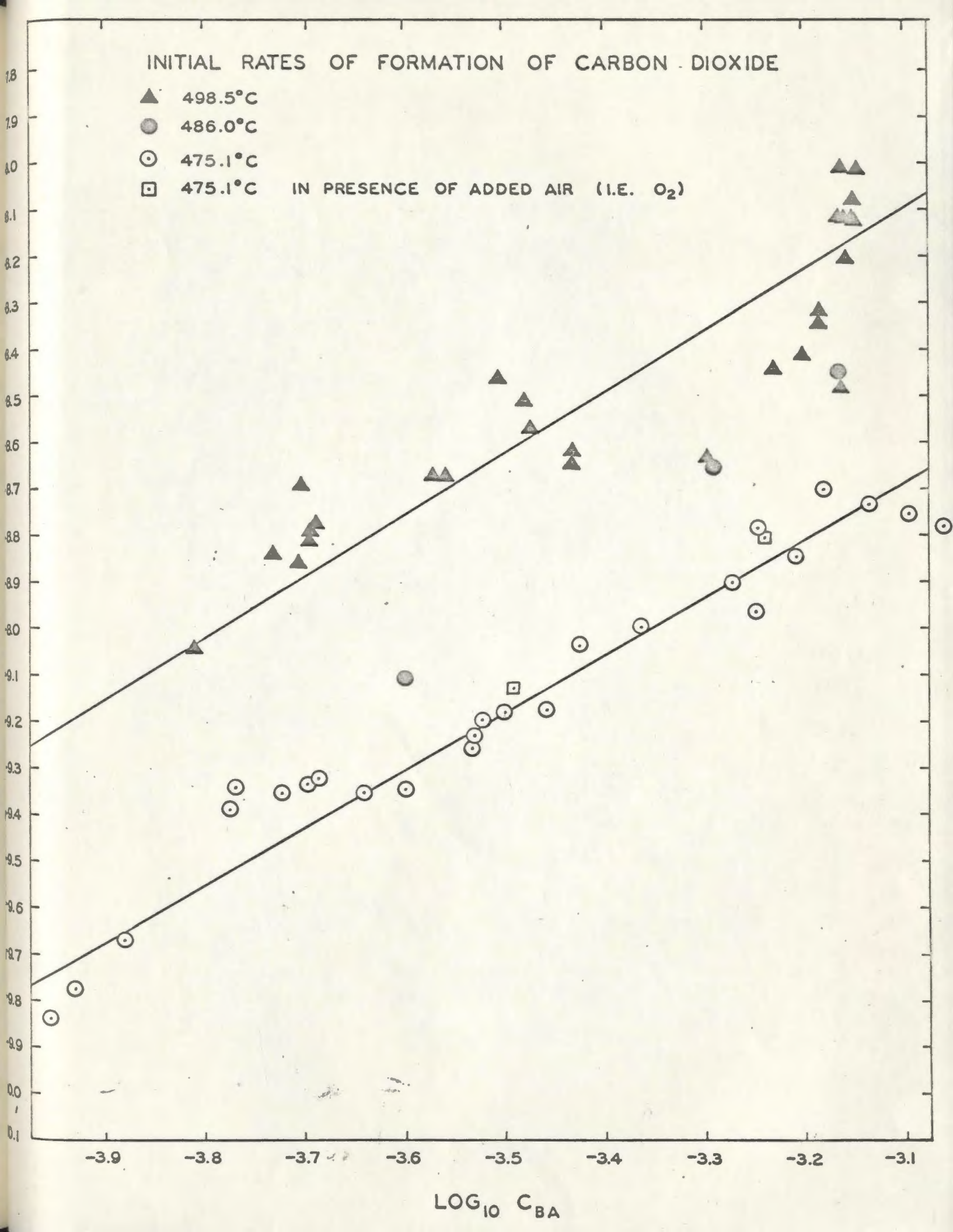

INITIAL RATES OF FORMATION OF CARBON DIOXIDE
498.5°C
486.0°C
475.1°C
475.1°C IN PRESENCE OF ADDED AIR (I.E. O_2)
-3.9
-3.8
-3.7
-3.6
-3.5
-3.4
-3.3
-3.2
-3.1
$LOG_{10}\ C_{BA}$

Figure 15

Initial Rates of Formation of Carbon Monoxide

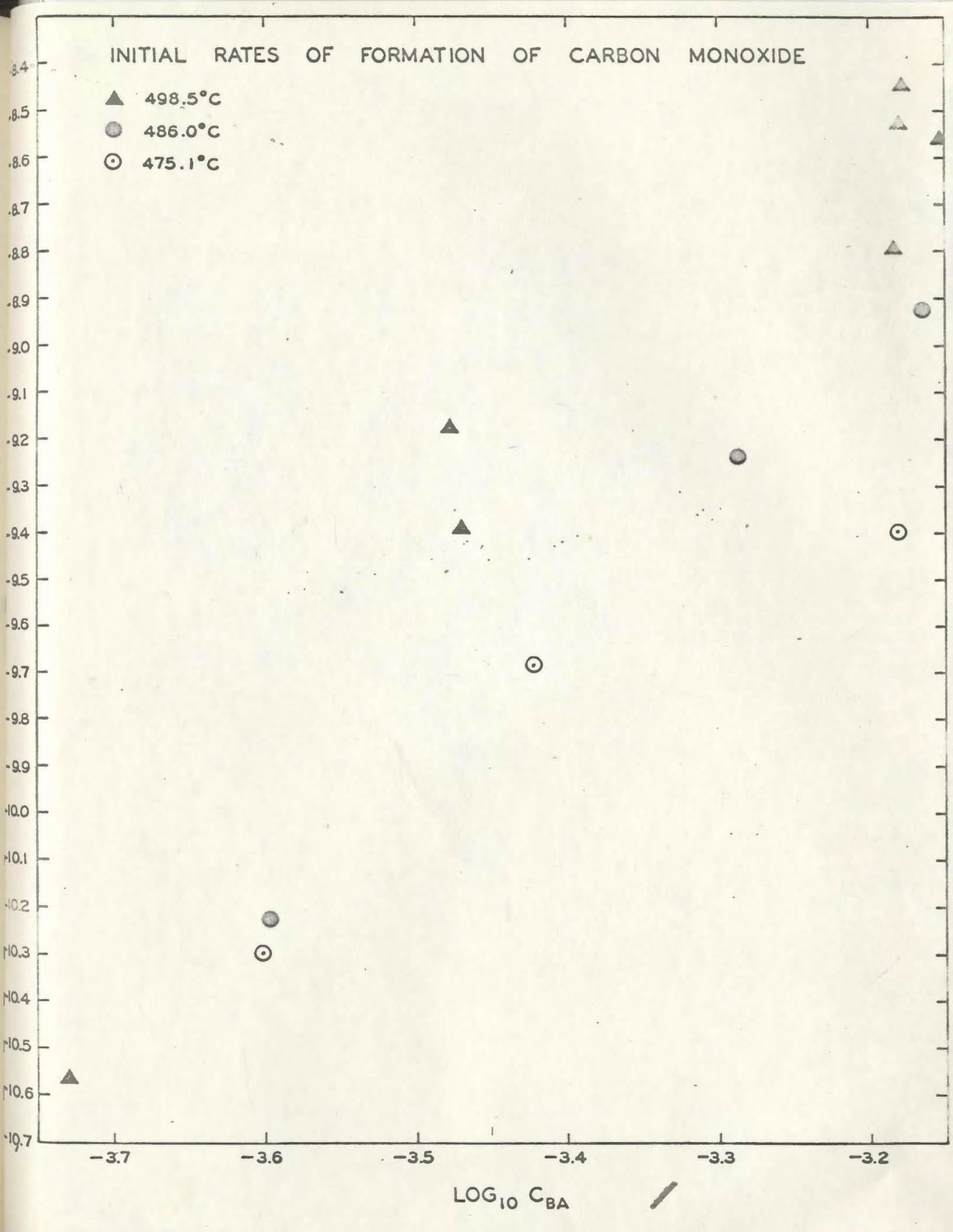

INITIAL RATES OF FORMATION OF CARBON MONOXIDE
498.5°C
486.0°C
475.1°C
-8.4
-8.5
-8.6
-8.7
-8.8
-8.9
-9.0
-9.1
-9.2
-9.3
-9.4
-9.5
-9.6
-9.7
-9.8
-9.9
-10.0
-10.1
-10.2
-10.3
-10.4
-10.5
-10.6
-10.7
-3.7
-3.6
-3.5
-3.4
-3.3
-3.2
LOG10 CBA

Figure 16

Initial Rates of Formation of Hydrogen

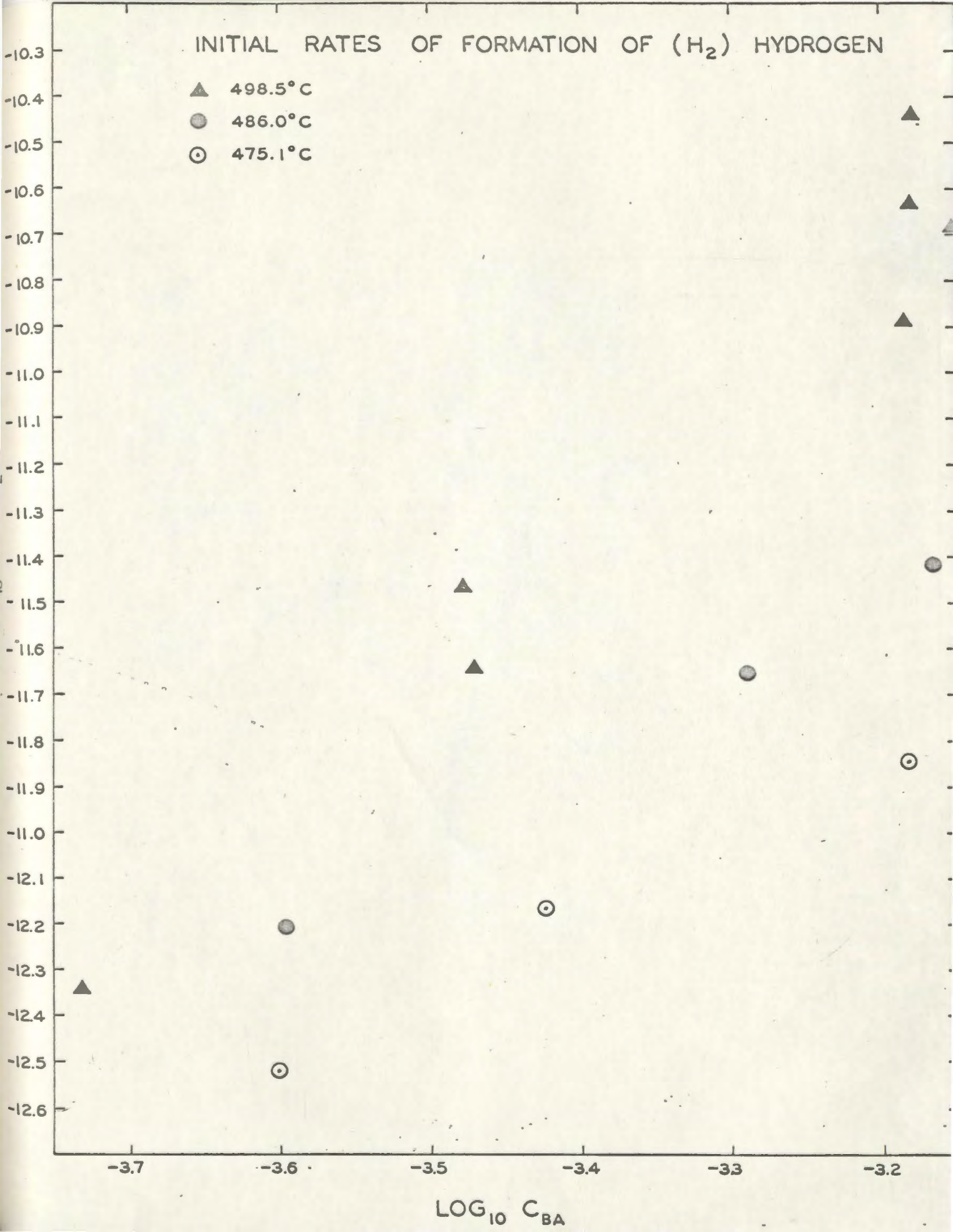

INITIAL RATES OF FORMATION OF (H_2) HYDROGEN
498.5°C
486.0°C
475.1°C
-10.3
-10.4
-10.5
-10.6
-10.7
-10.8
-10.9
-11.0
-11.1
-11.2
-11.3
-11.4
-11.5
-11.6
-11.7
-11.8
-11.9
-11.0
-12.1
-12.2
-12.3
-12.4
-12.5
-12.6
-3.7
-3.6
-3.5
-3.4
-3.3
-3.2
$LOG_{10}\ C_{BA}$

Figure 17

Initial Rates of Formation of CO + CO_2

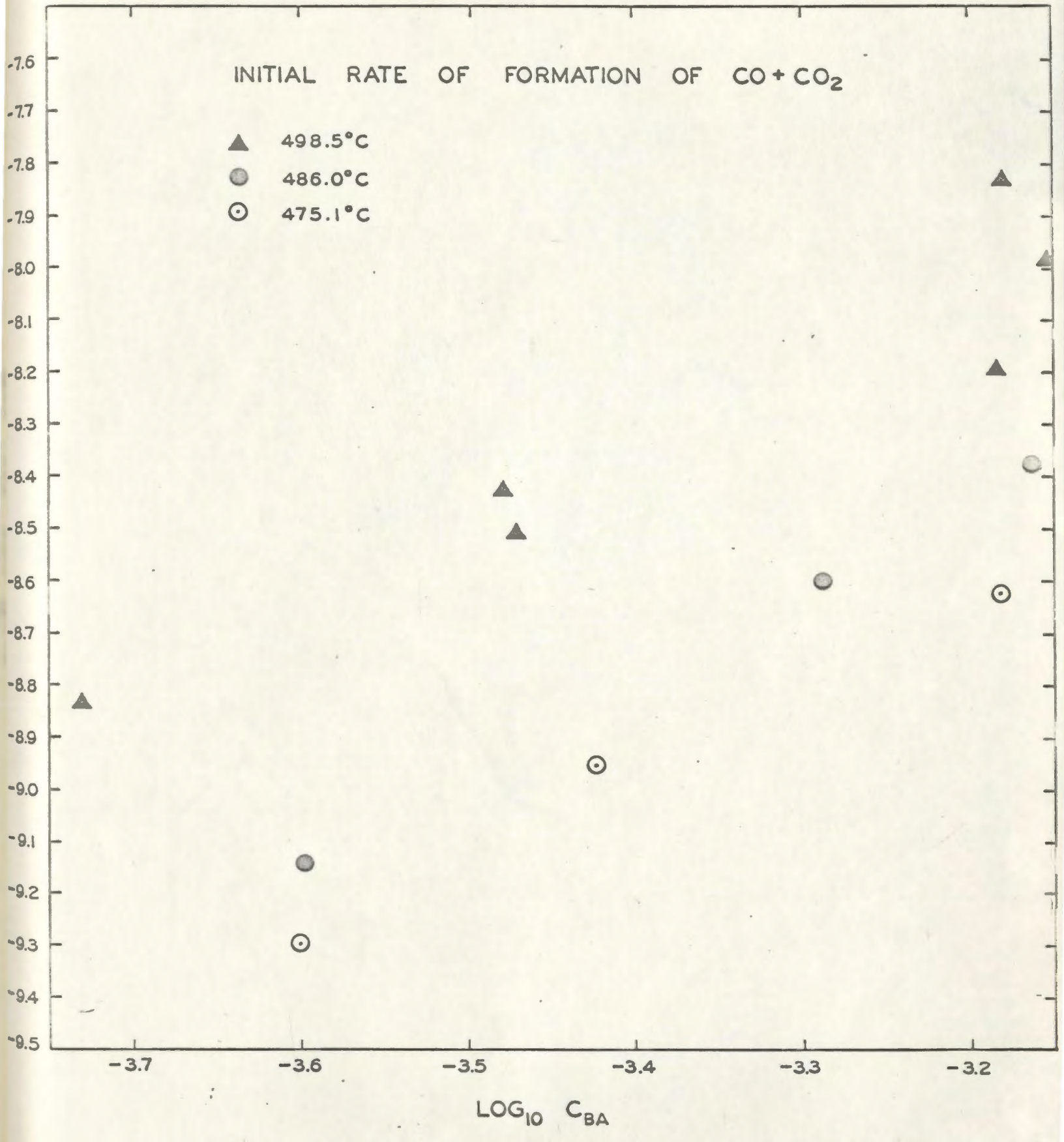

INITIAL RATE OF FORMATION OF CO + CO2
498.5°C
486.0°C
475.1°C
-7.6
-7.7
-7.8
-7.9
-8.0
-8.1
-8.2
-8.3
-8.4
-8.5
-8.6
-8.7
-8.8
-8.9
-9.0
-9.1
-9.2
-9.3
-9.4
-9.5
-3.7
-3.6
-3.5
-3.4
-3.3
-3.2
LOG10 CBA

Figure 18

Dependence of ratio $\frac{CO}{CO + CO_2}$ on

Benzoic Acid Pressure

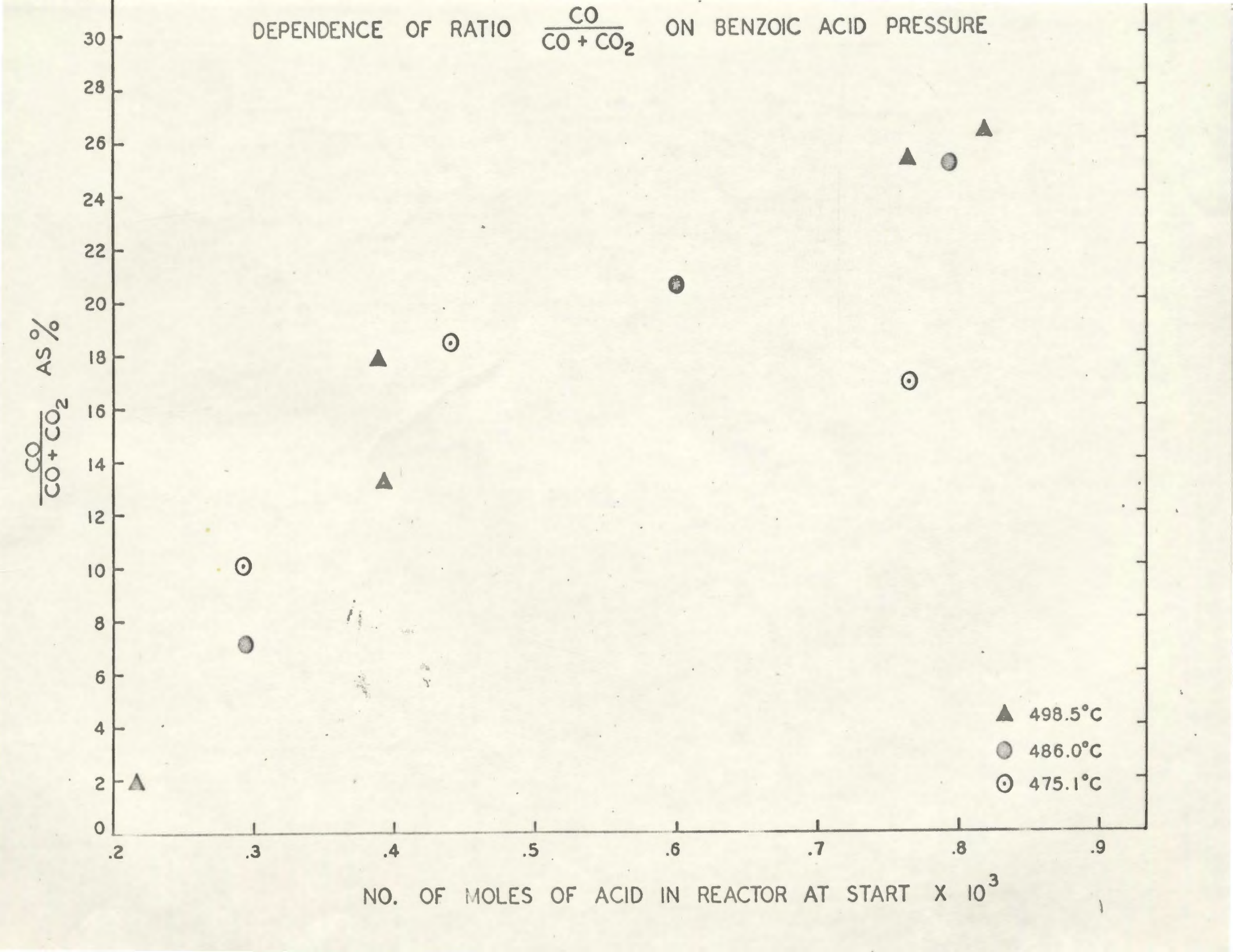

DEPENDENCE OF RATIO $\frac{CO}{CO + CO_2}$ ON BENZOIC ACID PRESSURE
$\frac{CO}{CO + CO_2}$ AS %
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
.2
.3
.4
.5
.6
.7
.8
.9
NO. OF MOLES OF ACID IN REACTOR AT START X 10^3
498.5°C
486.0°C
475.1°C

Figure 19

Plot of ratio $\frac{\text{Toluene-}d_8}{\text{Benzoic Acid}}$ vs. ratio $\frac{C_6H_5D}{C_6H_6}$

PLOT OF RATIO $\frac{d_8 \text{ TOLUENE}}{\text{BENZOIC ACID}}$ vs RATIO $\frac{C_6H_5D}{C_6H_6}$

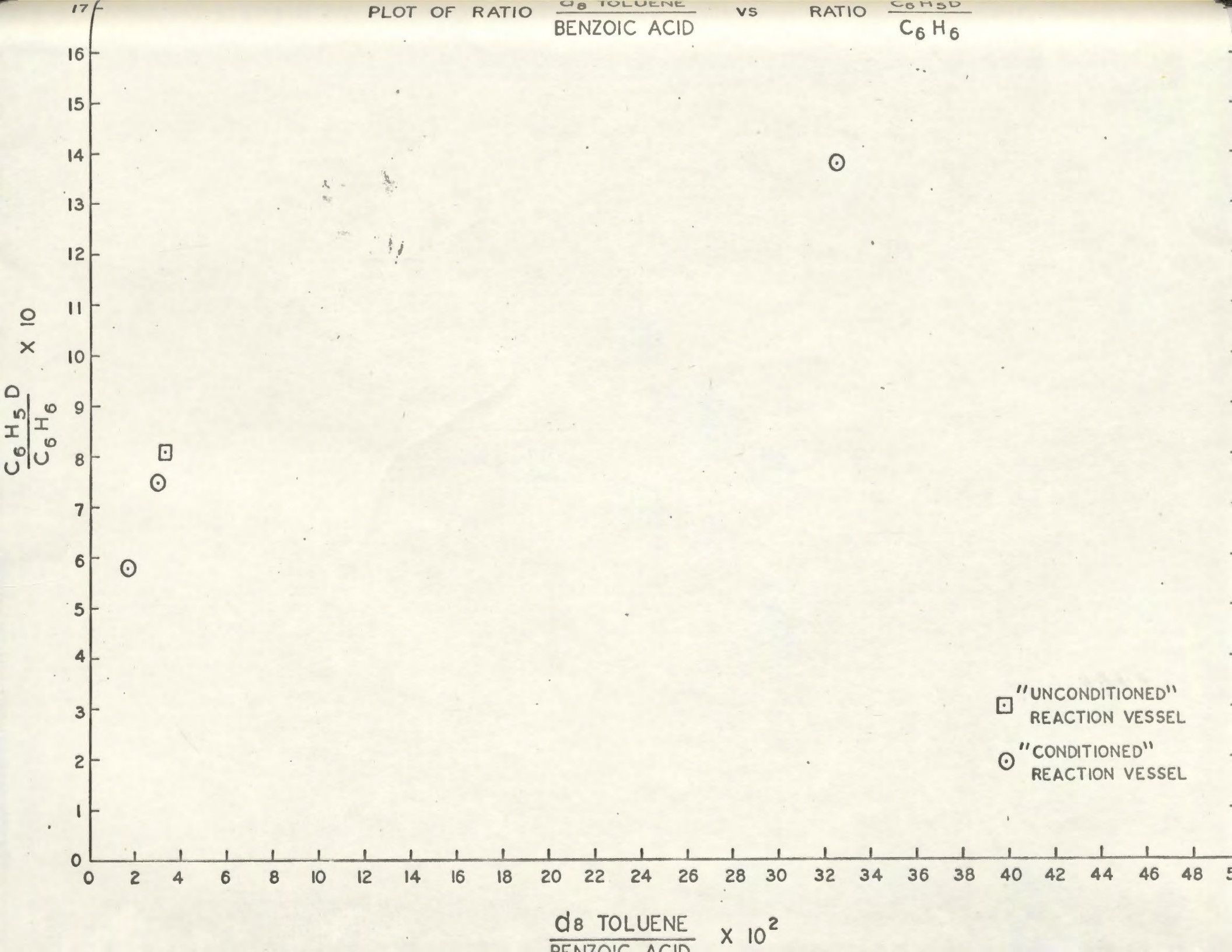
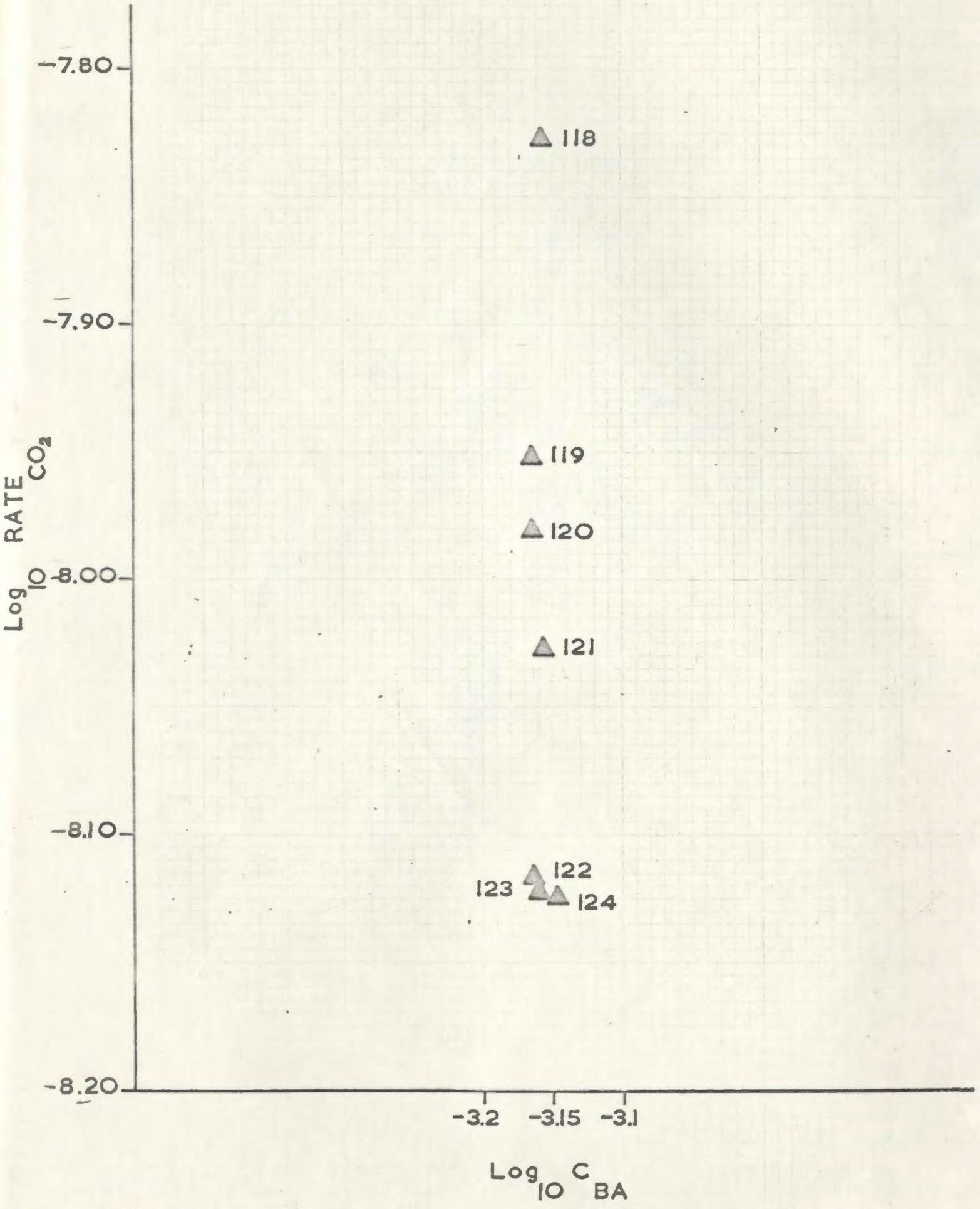


Figure 20

Effect of Conditioning Reaction Vessel on Rate of Reaction


-7.80
-7.90
-8.00
-8.10
-8.20
Log10 RATE CO2
118
119
120
121
122
123
124
-3.2
-3.15
-3.1
Log10 C BA

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13. a) T.E. Phipps, M.L. Spealman, and T.G. Cooke, J. Chem. Ed., 12, 321 (1935).

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APPENDIX

1. Reaction vessel filling procedure for experiments with toluene-d_8 and Benzoic acid:
   The acid was evaporated from reservoir 2 (Fig.1, page 90) through stopcock E into bulb 24 and then expanded into the reaction vessel 5. The pressure of acid was calculated from the known expansion factor from bulb 24 to the reaction vessel 5 at that temperature. Stopcock E was connected to the manifold directly above it. This manifold connects also to stopcocks A,B,C,D,F, G, and H. Bulb 24 was subsequently revacuated and filled with a known pressure of toluene-d_8, which was then expanded into the reaction vessel containing the acid.
   For experiments carried out in the presence of air, the air was added to the reaction vessel prior to the introduction of benzoic acid.

2. Melville and Gowenlock (Experimental Methods in Gas Reaction; MacMilland & Co., London (1964), p. 63) suggested that the maximum operating temperature for Apiezon T is 110°C and that for Dow Corning Silicone grease it was found necessary to regrease approximately once a month. As mentioned, p. 60, experiments were carried out to determine leak rate of air into the reaction vessel and the effect this air had on the reaction.

10. In studying the reaction $CO + O_2$ Gordon and Knipe (J.Phys.Chem.59, 1160 (1955)) heated the mixture of CO and O_2 to about 700° from room temperature at about 10 deg./ min. and held it at 700° for 5 minutes. About 3-4% CO_2 was generated. At higher temperatures more CO_2 is generated before explosion. Hoare and Walsh (Trans. Farad.Soc., 50, 37(1954)) admitted a dry mixture of $2CO + O_2$ at 55-60 mm. pressure to the reaction vessel at 450°C and heated to 525°C at which temperature still no slow oxidation occurred. Slow reaction only began when supplementary gases such as H_2CO, HCl, CH_4, H_2, H_2O_2, argon, or combinations of these gases were admitted to the silica reaction vessel. Semenov (Chem.Revs., 6,347 (1929)), in studying the explosion of $CO + O_2$ found the thermal reaction below the explosion point to be very slow. The substitution of air instead of O_2 gave the same value for the pressure above which no explosion could occur (P_{max} here meaning total pressure $CO + O_2 + N_2$). It would appear that the reaction of CO and O_2 to give CO_2 may take place at the temperatures used in this study of the benzoic acid decomposition but if so the extent of it is very small. This would seem to be born out by the results of reactions carried out in the presence of added air (see p.60).

12. The idea of a relationship for CO/CO_2 results from phenylacetic acid, diphenylacetic acid, and benzoic acid was investigated since, if CO and CO_2 came mainly

decomposition of carboxyl radical, approximately the same ratio, CO/CO_2, should be found for all decarboxylations. However, no such relationship was found to exist since, in the benzoic acid case, most of the CO_2 produced does not arise from decomposition of the carboxyl radical.

13. (continued). Further discussion of reactions in presence of toluene-d_8:.

The expression for $\frac{d\,[C_6H_5D]}{d\,[C_6H_6]}$ derived on p.76 from expressions (A) and (B) (also on p.76) can be derived by considering reactions (5)-(12) (p.79-80), giving

$$\frac{d\,[C_6H_5D]}{d\,[C_6H_6]} = \frac{k_A\,[C_6D_5CD_3]}{k_B\,[C_6H_5COOH]}$$

Early in the reaction $[C_6H_5D] / [C_6H_6]$ would be a linear function of $[C_6D_5CD_3] / [C_6H_5COOH]$ and later in the reaction $[C_6H_5D] / [C_6H_6]$ would be even greater than that early in the reaction because the $[C_6D_5CD_3] / [C_6H_5COOH]$ ratio is increasing as the reaction proceeds (since $C_6D_5CD_3$ is in excess and C_6H_5COOH is reacting). Since it was found that the $[C_6H_5D] / [C_6H_6]$ ratio was much less sensitive to $[C_6D_5CD_3] / [C_6H_5COOH]$ than required by the radical mechanism proposed it was assumed that this was not the only mechanism.

The results appear to be consistent with a contribution from a molecular elimination reaction producing CO_2 and suggest in experiment 147 which uses the highest $[C_6D_5CD_3]$ / $[C_6H_5COOH]$ that ratio $[C_5H_5D]$ / $[C_6H_6]$ is at or near a maximum value, most of the phenyl radical produced having reacted with toluene-d_8. With the combined radical and molecular mechanism inhibition by toluene-d_8 should be observed. At a high pressure of toluene-d_8 the reaction left uninhibited should be the molecular reaction and the quantity of C_6H_5D produced should then be equal to the quantity of phenyl radical produced. However, in the absence of toluene-d_8 a lot more phenyl radical could be produced via the chain. From Table XIV it is difficult to come to any conclusions about the effect of the added toluene-d_8 on the rate of formation ofCO_2 in conditioned vessels, the effect (if there is one) being smaller than the experimental error. On the other hand the formation of CO is definitely inhibited in the presence of toluene-d_8. With the existing data it is difficult to explain the reason why one should be inhibited and the other not.

In the unconditioned reaction vessel the presence of toluene-d_8 appeared to slightly accelerate the formation of CO_2 and CO and to slightly increase the $CO/(CO + CO_2)$ ratio; perhaps at high toluene-d_8 pressures the total reaction is accelerated. The results indicate some decomposition of toluene-d_8 possibly leading to a chain

reaction initiated by $.CD_3$ or D. As with all experiments in unconditioned reaction vessels that were carried out in the presence of toluene-d_8, 140, was considerably faster than a comparable experiment in a conditioned vessel, 139.

It appears that conditioning of the reaction vessel suppresses a reaction producing CO_2 (presumably at the surface) since $CO/(CO + CO_2)$ is lower in the unconditioned vessel. The ratio $[C_6H_5D] / [C_6H_5]$ is approximately the same in both conditioned and unconditioned vessels (experiments 139, 140). If there is a fast molecular reaction producing CO_2 in the unconditioned vessel we would expect the ratio of benzenes to be lower than in the conditioned vessel. This suggests that both the reactions

$$C_6H_5COOH \rightarrow C_6H_6 + CO_2$$

$$C_6H_5COOH \rightarrow C_6H_5. + , COOH$$

occur at the surface in unconditioned vessels. It would also seem that both reactions take place in the same proportions but to a greater extent than in conditioned vessels, i.e. lack of conditioning makes both reactions proceed faster. The carboxyl radical produced in the above reaction would have to yield more CO in the conditioned than in the unconditioned vessel since the ratio $CO/(CO + CO_2)$ is higher in the case of conditioning.

The reaction in the presence of toluene-d_8 deserves considerable further study.

TABLE VI

Product Analysis

Run	Calculated from $\frac{CO + CO_2}{(C_6H_5COOH)}$	from titration
Temp: 498.5°C		
93	25.58	31.93
97	5.13	
102	72.25	
110	93.00	95.80
112	4.33	4.52
116	21.29	28.55
127	41.66	41.68
151	37.93	37.88
Temp 475.1°C		
36	90.90	
33	.401	
32	.38	
31	.76	
30	3.75	
29	.25	
21	88.41	88.50
20	88.62	88.70

Table VI (cont'd)

19	107.0
18	102.0
37	2.72
38	1.45
39	1.30
40	1.21
41	1.32
42	1.22
43	.996
45	2.24
46	1.41
47	.88
48	1.14
49	